

WET DR

MIXED TO M

End-Product and Processing Requirements

Under a fixed
DAY 11/1/1941
to be a good
understanding

The fast, reliable service please contact:

UNITED CARGO COMPANY,

115 PARK AVENUE, NEW YORK 22.

ALSO OFFICES IN LONDON, NEW YORK

AND OTHER PORTS

**No matter where in the world you are,
Cabot can serve you better**



Cabot produces more different grades of carbon black than anyone else — and sells more — not only in the U. S. but throughout the world. On all six continents. In 58 different countries.

Cabot has more production facilities — abroad — than anyone else. Ships from more countries. Sells in more currencies. And Cabot is continually establishing new plants.

That's why Cabot can serve your carbon black needs better than anyone else — internationally.

Sales representatives in all principal cities of the world



CABOT CORPORATION

125 HIGH STREET, BOSTON 10, MASSACHUSETTS

AKRON • CHICAGO • DALLAS • LOS ANGELES • NEW BRUNSWICK • NEW YORK

Cabot Argentina S.A.
Sarmiento 930, Buenos Aires, Argentina

Cabot Carbon of Canada, Ltd.
121 Richmond Street West, Toronto 1, Ontario, Canada

Cabot Carbon Limited
62 Brompton Road, London, S.W. 3, England

Cabot France S.A.
45, rue de Courcelles, Paris 8, France

Cabot Italiana S.p.A.
Via Larga 19, Milano, Italy

Cabot Europa
45, rue de Courcelles, Paris 8, France

Australian Carbon Black Pty. Limited
Millers Road, Altona, Victoria, Australia (jointly owned)

REGAL BLACKS:	Regal 600	Regal 300	Regal SRF	Regal 99 FF
FURNACE BLACKS:	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Sterling V GPF
	Vulcan SC SCF	Vulcan C CF	Sterling SO FEF	Sterling NS SRF
	Sterling L HMF	Sterling LL HMF	Sterling S SRF	Gastex SRF
	Pelletex SRF	Pelletex NS SRF	Sterling R SRF	Sterling FT FF
THERMAL BLACKS:	Sterling 99 FF	Vulcan XC-72 ECF		
	Sterling FT	Sterling MT	Sterling MT NS	
	Sterling MT FF	Sterling MT NS FF		
CHANNEL BLACKS:	Spheron 9 EPC	Spheron 6 MPC		

RUBBER CHEMISTRY AND TECHNOLOGY

Published in Five Issues (January-March, April-June, July-September,
October-November & December) under the Auspices of the Division
of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor.....	DAVID CRAIG	Business Manager.....	GEORGE HACKIM
Associate Editor.....	S. D. GEHMAN	Advertising Manager....	GEORGE HACKIM
Associate Editor.....	H. J. J. JANSSEN	Treasurer.....	D. F. BEHNEY

Vol. XXXIV

December 1962

No. 5

CONTENTS

	<i>General Section</i>	PAGE
Officers		iii
Future Meetings		vi
Sponsored Rubber Groups		vii
Chemical Institute of Canada Rubber Division and Sponsored Rubber Groups ..		xi
Election Results		xii

Papers

The Biosynthesis of Rubber. P. FOURNIER AND TUONG-CHI-CUONG	1229
Kinetic Studies of the Vulcanization of Natural and Synthetic Rubbers. WALTER SCHEELE	1306
Oil-Extended Rubbers. E. B. STOREY	1402
Carbon Black—Latex Masterbatches. H. J. J. JANSSEN AND K. V. WEINSTOCK ..	1485
Recent Developments in Synthetic Rubber Latex. L. H. HOWLAND AND R. W. BROWN	1501
Fluorine-Containing Elastomers. J. C. MONTERMOSO	1521
Instrumental Methods for the Analysis of Polymeric Materials. J. MITCHELL, JR. AND S. S. LORD, JR.	1553
Nuclear Magnetic Resonance Studies of Elastomers. W. P. SLICHTER	1574
Index	1601

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues (\$6.00 per year) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of \$8.50 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at the subscription price of \$9.50 per year.


To these charges of \$6.00, \$8.50 and \$9.50, respectively, per year, postage of \$1.45 per year must be added for subscribers in Canada, and \$1.60 per year for those in all other countries not United States possessions.

All applications to become Members or Associates of the Division of Rubber Chemistry, with the privilege of receiving this publication, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, D. F. Behney, Harwick Standard Chemical Co., 60 South Seiberling Street, Akron 5, Ohio.

All correspondence concerning subscriptions should be directed to the Business Manager of RUBBER CHEMISTRY AND TECHNOLOGY, Mr. George Hackim, c/o The General Tire & Rubber Company, Chemical Division, Akron 9, Ohio.

Articles, including translation and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

For rubber products that are better Choose the proper Philblack* letter



Each of the four Philblacks offers its own outstanding advantages. Use them separately, or in combination for greater recipe flexibility. Your Phillips technical representative will be glad to advise on recipes, or help you with any operational problem.

LET ALL THE PHILBLACKS WORK FOR YOU!

A **PHILBLACK A, EXTRUSION FURNACE BLACK.** Excellent tubing, molding, calendering, finish! Mixes easily, disperses heat. Non-staining.

O **PHILBLACK O, ABRASION FURNACE BLACK.** For long, durable life. Good conductivity. Excellent flex life and hot tensile. Easy processing.

I **PHILBLACK I, INTERMEDIATE SUPER ABRASION FURNACE BLACK.** Superior abrasion. More tread miles at moderate cost.

E **PHILBLACK E, SUPER ABRASION FURNACE BLACK.** Toughest black yet! Extreme resistance to abrasion.

*A trademark



PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Sales Div., 318 Water St., Akron 8, Ohio

Sales Offices: Akron, Chicago, Dallas, Providence and Trenton

West Coast: Harwick Standard Chemical Company, Los Angeles, California

Export Sales: Phillips Petroleum International Corporation, Sumatrastrasse 27, Zurich 6, Switzerland
Distributors of Phillips Chemical Company Products, 80 Broadway, New York 5, N. Y.



These accessories are right in the swim ...at a profit...with PLIOFLEX!



"Big" just begins to describe the market for fins, masks and other rubber swimming accessories. That's why competition is tough. To stay in the swim—at a profit—a manufacturer must offer quality—and keep costs down.

One leading manufacturer does both, with PLIOFLEX 1502 and 1773.

These low-cost rubbers offer maximum uniformity—minimize rejects. They're rubbers of *assured processability*—deliver the same quality every time.

To improve your products, consider PLIOFLEX. We have more than 20 types. For details, write:

Goodyear, Chemical Division,
Dept. L-9430,
Akron 16, Ohio.



Photograph taken with cooperation of
Globe Rubber Products Corp., Philadelphia, Pa.

Plioflex—T. M. The Goodyear Tire & Rubber Company, Akron, Ohio

GOODYEAR

CHEMICAL DIVISION

From Eastman...

A family of fine products to serve the rubber industry

ANTIOXIDANTS

TENAMENE® 3

2,6-Di-tert-butyl-p-cresol.
An excellent non-discoloring and non-staining antioxidant of low odor and toxicity for light-colored rubber and synthetic elastomers.

HYDROQUINONE MONOMETHYL ETHER

Valuable antioxidant and polymerization inhibitor.

2,5-DI-tert-BUTYLHYDROQUINONE

Effective in rubber and synthetic elastomers; also an excellent polymerization inhibitor.

TENOX®

A series of non-discoloring, food-grade antioxidants.

TECQUINOL® (Hydroquinone, tech.)

Retards polymerization of styrene and gelation of rubber sols.

CELLULOSES

CELLULOSE ACETATE BUTYRATE

For use in abrasion-resistant lacquers for rubber articles. Flow and bodying agent for coatings made from urethane.

INTERMEDIATES

Reactants in the preparation of antioxidants and accelerators.

ACETALDEHYDE

ACETONE

CROTONALDEHYDE

ISOBUTYRALDEHYDE

PROPIONALDEHYDE

n-BUTYRALDEHYDE

CROTONIC ACID

HYDROQUINONE (tech.)

ISOBUTYRONITRILE

Facilitates reclamation of scrap rubber. Esters for softening agents and solvents.

DAC-B

Preparation of hydrocarbon resins

DI-(β -HYDROXY-ETHYL) ETHER OF HYDROQUINONE

Cross-linking agent for polyurethanes.

NEOPENTYL GLYCOL

Polyesters of outstanding stability for polyurethane.

ANTIOZONANTS

EASTOZONE® 32

Especially useful in static exposure applications.

ADHESIVES

EASTMAN 910 ADHESIVE

A fast-setting adhesive for strong rubber-to-rubber and rubber-to-metal bonds.

WAXES

Non-emulsifiable, low-molecular-weight, polyethylene resins for use as calender release agents in milling.

EPOLENE LV

EPOLENE® N

EPOLENE HD

EPOLENE C

PLASTICIZERS

DIBUTYL PHTHALATE

DI-(2-ETHYLHEXYL) PHTHALATE

DI-(2-ETHYLHEXYL) AZELATE

DIBUTYL SEBACATE

POLYMERIC PLASTICIZER NF-10

Eastman

CHEMICAL PRODUCTS, INC.

KINGSPORT, TENNESSEE

Subsidiary of Eastman Kodak Company

A new booklet containing more information on the products described here has just been published. For your copy, write to

SALES OFFICES: Eastman Chemical Products, Inc., Kingsport, Tennessee; Atlanta; Boston; Buffalo; Chicago; Cincinnati; Cleveland; Detroit; Greensboro, N. C.; Houston; Kansas City, Mo.; New York City; Philadelphia; St. Louis. West Coast: Wilson & Goo. Moyer & Company, San Francisco; Los Angeles; Portland; Salt Lake City; Seattle.

Reliable, Consistent Test Results With . . .

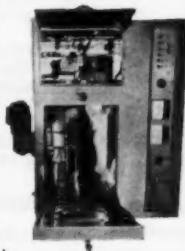
OREC 0300 Automatically Controlled Ozone Test Chambers

REPRESENTATIVE CUSTOMERS UTILIZING OREC OZONE TEST EQUIPMENT

Anaconda Wire & Cable Co.
E. I. DuPont de Nemours & Co.
Esso Research & Engineering Co.
Firestone Industrial Products
General Electric Company
General Tire & Rubber Co.
B. F. Goodrich Research Center
Goodrich Gulf Chemical Co.
Goodyear Tire & Rubber Co.
General Motors Corporation
Phelps Dodge Corporation
Phillips Chemical Co.
Texas U.S. Chemical Co.
TLARGI, U.S.C.
U. S. Rubber Company
Shell Chemical Corporation



Orec 0300 Series employ an "electronic-chemical loop feed back servo system to achieve and precisely maintain chamber ozone concentrations.



Orec 0300 with Dynamic Stretching Apparatus.
* patent pending

OZONE:

- TEST CHAMBERS, 6 MODELS
- AUTOMATIC CONTROL SYSTEMS
- RECORDING INSTRUMENTATION
- STRETCHING APPARATUS
- MEASUREMENT INSTRUMENTATION
- GENERATORS
- TESTING SERVICE
- RESEARCH & DEVELOPMENT

Write for illustrated brochure

Ozone Research and Equipment Corporation

3840 North 40th Avenue

Phoenix, Arizona

Naugatuck RUBBER CHEMICALS

ACCELERATORS

Thiazoles	Thiurams	Dithiocarbamates	Aldehyde Amines
M-B-T	Tuex [®]	Arazate [®]	Beutene [®]
M-B-T-S	Ethyl Tuex [®]	Butazate [®]	Hepteen Base [®]
O-X-A-F	Monex [®]	Butazate [®] 50-D	Trimene Base [®]
DELAC-S	Pentex	Ethazate [®]	Trimene [®]
	Pentex Flour	Ethazate 50-D	
		Methazate [®]	
	Xanthates	Vulcanizing Agents	
	C-P-B [®]	G-M-F-SD	
	Z-B-X	Dibenzo G-M-F-SD	

ACTIVATOR

D-B-A Accelerator

ANTIOXIDANTS

Discoloring	Nondiscoloring	Semi-nondiscoloring	Antiozonants
Aminox [®]	Polygard [®]		Flexzone 3-C
Aranox [®]	Naugawhite	Octamine	Flexzone 6-H
B-L-E-25	Naugawhite Powder	Betanox Special [®]	
Flexamine G			
V-G-B [®]			

BLOWING AGENTS

Celogen[®] Celogen-AZ[®]

SUNPROOFING WAXES

Sunproof [®] Regular	Sunproof [®] Improved	Sunproof [®] Jr.
Sunproof [®] -713	Sunproof [®] Super	Sunproof Extra

MISCELLANEOUS SPECIAL PRODUCTS

BWH-I—mixture of oils	THIOSTOP K—40% aqueous solution of potassium dimethyl dithiocarbamate
DDM—dodecyl mercaptan	
LAUREX [®] —zinc laurate	THIOSTOP N—35% aqueous solution of sodium dimethyl dithiocarbamate
PROCESS STIFFENER #710—26.4% hydrazine salt and 73.6% inert mineral filler	
TONOX—p,p'-diaminodiphenylmethane	

RETARDERS

RETARDER E-S-E-N RETARDER J

* available in Nauget form



Naugatuck Chemical

Division of United States Rubber Company

160 R Elm Street

Naugatuck, Connecticut



Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latexes
CANADA: Naugatuck Chemicals Division, Dominion Rubber Co., Ltd., Elmira, Ontario • CABLE: Rubexport, N.Y.

DU PONT CHEMICALS and COLORS

DEPENDABLE IN PERFORMANCE...UNIFORM IN QUALITY

ACCELERATORS

Accelerator No. 8
Accelerator 552
Accelerator 808
Accelerator 833
Conac S
Conac S Grains
DOTG
Thionex Grains

Thiuram E
Thiuram E Grains
Thiuram M
Thiuram M Grains
Zenite
Zenite Special
Zenite A
Zenite AM

ORGANIC ISOCYANATES

Hylene* M
Hylene* M-50
Hylene* MP
Hylene* T
Hylene* TM
Hylene* TM-65

PEPTIZING AGENTS

Endor
RPA No. 2
RPA No. 3
RPA No. 3 Concentrated
RPA No. 6
RR-10

ANTI-OXIDANTS

Akroflex C Pellets
Akroflex CD Pellets
Antox
Neozone A Pellets
Neozone C
Neozone D
Permalux

Thermoflex A Pellets
Zalba
Zalba Special

RECLAIMING CHEMICALS

RPA No. 3
RR-10

AQUAREXES (MOLD LUBRICANTS AND STABILIZERS)

Aquarex D
Aquarex G
Aquarex L
Aquarex MDL
Aquarex ME
Aquarex NS
Aquarex SMO
Aquarex WAQ

BLOWING AGENTS

Unicel ND
Unicel NDX
Unicel S

RUBBER DISPERSED COLORS

Rubber Red PBD
Rubber Red 2BD
Rubber Yellow GD
Rubber Green GSD
Rubber Green FD
Rubber Blue PCD
Rubber Blue GD
Rubber Orange OD

SPECIAL-PURPOSE CHEMICALS

BARAK—Retarder activator for thiazole accelerators

Copper inhibitor 50—Inhibits catalytic action of copper on elastomers

ELA—Elastomer lubricating agent

HELIOZONE—Sun-checking inhibitor

NBC—Inhibits weather and ozone cracking of SBR compounds

RETARDER W
Retarder-activator for acidic accelerators

* REG. U. S. PAT. OFF.

DISTRICT OFFICES

Akron 8, Ohio, 40 E. Buchtel Ave. at High St. POrtage 2-8461
Atlanta, Ga., 1261 Spring St., N.W. TRinity 5-5391
Boston 10, Mass., 140 Federal St. HANcock 6-1719
Charlotte 1, N. C., 427 W. 4th St. FRanklin 5-5561
Chicago 3, Ill., 7 South Dearborn St. ANdover 3-7000
Detroit 35, Mich., 13000 W. 7-Mile Rd. UNiversity 4-1963
Houston 27, Texas, 2601A West Grove Lane MOhawk 7-7429
Los Angeles 58, Calif., 2930 E. 44th St. LUdlow 2-6464
Palo Alto, Calif., 701 Welch Rd. DAvenport 6-7550
Trenton 8, N. J., 1750 N. Olden Ave. TUxedo 2-8050
In New York call Walker 5-3290
In Canada contact: Du Pont Company of Canada Limited

E. I. du Pont de Nemours & Co. (Inc.)
Elastomer Chemicals Department

Wilmington 98, Delaware



Better Things for Better Living
... through Chemistry

QUALITY PRODUCTS for the RUBBER INDUSTRY

General Tire's Chemical Division is constantly aware of the needs of the rubber industry, and provides these specially-formulated products to meet those needs. Write or call for further information and generous samples.

RUBBER CHEMICALS:

- GEN-TAC** • Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.
- KO-BLEND** • Latex-compounded masterbatch, 85% insoluble sulfur colloiddally dispersed in SBR latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.
- KURE-BLEND MT** • 50 SBR—50 TMTD latex-compounded masterbatch. Gives faster, more even dispersion, allowing full advantage of TMTD accelerator. Assures uniform cure, at no premium cost.

RUBBER:

- GENTRO** • Top-quality cold SBR Polymers.
- GENTRO-JET** • Cold and oil-extended black masterbatches, for easier processing and more efficient production.

LATICES:

- GEN-FLO** • Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.
- ACRI-FLO** • Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

PVC RESINS:

- VYGEN** • a complete family of top-quality, versatile resins formulated to meet specific needs.

THE GENERAL TIRE & RUBBER COMPANY
CHEMICAL DIVISION • AKRON, OHIO

Creating Progress Through Chemistry



**AVAILABLE FROM THE TREASURER
DIVISION OF RUBBER CHEMISTRY
*AMERICAN CHEMICAL SOCIETY***

"Introduction to Rubber Technology" by Maurice Morton
\$7.00 per copy to *Members and Associates* only. All
others (including subscribers) may purchase direct from
Reinhold Publishing Corp., 430 Park Avenue, New York.

Proceeding of International Rubber Conference, 1959.
\$5.00.

Back issues of Rubber Chemistry and Technology are
also available, at prices ranging from \$2.00 per copy to
\$8.00 per copy.

Donations of certain issues in short supply, to the Division, would
be appreciated. These are Vol. No. 1 (1928), Vol. XXX, No. 3
(1957) and Vol. XXXII, No. 1 (1960).

*Checks payable to the Division of Rubber Chemistry, A. C. S.,
should accompany the order and be sent to:*

**D. F. Behney
c/o Harwick Standard Chemical Co.
60 South Seiberling Street
Akron 5, Ohio**

Shopping list for the Rubber Compounder

CYANAMID RUBBER CHEMICALS

ACCELERATORS

THIAZOLES

MBT (Mercaptobenzothiazole)
MBT-XXX (Specially refined — odorless)
ZMBT (Zinc salt of 2-mercaptobenzothiazole)

MBTS (Benzothiazyl disulfide)
MBTS Pellets

CYDAC® Accelerator Flaked
NOBS® No. 1 Accelerator
NOBS SPECIAL Accelerator
DIBS® Accelerator

GUANIDINES

DPG (Diphenylguanidine)
Regular or Dustless
DOTG (Dionthotolylguanidine)
Regular or Dustless

ACCELERATOR 49

THIAZOLINE

2-MT (2-Mercaptothiazoline)

THIURAMS

CYURAM*MS (Tetramethylthiuram monosulfide)
CYURAM*DS (Tetramethylthiuram disulfide)

Accelerators—continued:

DITHIOCARBAMATES

CYZATE*B (Zinc Dibutyl
Dithiocarbamate—
50% Aqueous Dispersion)
CYZATE*E (Zinc Diethyl
Dithiocarbamate—
50% Aqueous Dispersion)

ANTIOXIDANTS

ANTIOXIDANT 2246®
ANTIOXIDANT 415®

DEPTIZERS

PEPTON® 22 Plasticizer
PEPTON® 65 Plasticizer
PEPTON® 65B Plasticizer

RETARDER

RETARDER PD

AEROSOL

SURFACE ACTIVE AGENTS

* TRADEMARK

These high-quality products are available
from any of our conveniently located warehouses.
To order call your nearby American Cyanamid Office.
For technical literature on the above products, address—

CYANAMID

AMERICAN CYANAMID COMPANY

Rubber Chemicals Department • Bound Brook, New Jersey

SALES OFFICES AND WAREHOUSES: 340 South Broadway, Akron 8, Ohio • Bound Brook, New Jersey

• 3505 North Kimball Avenue, Chicago 80, Illinois • 2300 S. Eastern Ave., Los Angeles 22, California •

40 Fountain St., Providence 3, Rhode Island • 5180 Peachtree Industrial Blvd., Chamblee, Georgia (Atlanta 2)

• 1096 Commonwealth Ave., Boston 15, Massachusetts • 3143 N. W. Yeon Ave., Portland 10, Oregon

Hycar Rubber

REG. U. S. PAT. OFF.

- EXCEPTIONAL RESISTANCE TO OILS, FUELS, SOLVENTS
- LONG WEARING
- EASY TO PROCESS

HYCAR 1001, 1041, 1051. High acrylonitrile content, best oil and fuel resistance. Hycar 1051 provides superior processing qualities.

HYCAR 1411. Special finely divided powder type nitrile rubber, for use in modification of phenolic and vinyl resins.

HYCAR 1002, 1042, 1052. Medium high acrylonitrile content. Hycar 1002 provides best water resistance of all nitrile rubbers. Hycar 1052 provides excellent processing characteristics.

HYCAR 1312. Liquid nitrile polymer of medium acrylonitrile type. A non-extractable, non-migrating, non-volatile plasticizer. Can be cured to a hard rubber state.

HYCAR 1432. A low-temperature-polymerized, directly soluble polymer in crumb form.

HYCAR 1072. Excellent compatibility with vinyl and phenolic resins. Improved resistance to brittleness at low temperature, good hot tear and outstanding abrasion resistance.

HYCAR 1043, 1053. Medium acrylonitrile content. Improved low temperature properties. Hycar 1053, improved processing, excellent for extrusion.

HYCAR 1014. Low acrylonitrile content. Excellent low-temperature flexibility at sacrifice in oil and solvent resistance.

HYCAR 4021 (PA-21). Polyacrylic acid ester polymer. For air and hot oil applications above 300°F.

HYCAR 2252. Brominated butyl polymer. In addition to typical butyl properties, it cures faster, requires less acceleration, and is compatible with other rubbers.

GOOD-RITE® PRODUCTS

GOOD-RITE 2007, 2057. Good-rite 2007 (Good-rite Resin 50) reinforcing agent and processing aid for use with SBR and other rubbers. Used in highly loaded or low-gravity hard compounds requiring toughness, high abrasion, excellent flex life. Good-rite 2057, a masterbatch of equal parts SBR and Good-rite 2007.

GOOD-RITE VULTROL. Prevents scorching of SBR and crude rubber stocks; no sacrifice in rate of cure.

• For further information, write Dept. ME-5, B.F. Goodrich Chemical Company, 3135 Euclid Avenue, Cleveland 15, Ohio. In Canada: Kitchener, Ontario.

B.F. Goodrich Chemical

a division of The B.F. Goodrich Company

B.F. Goodrich

COLUMBIAN offers an outstanding carbon black for every rubber need...



STATEX® 160 SAF Super Abrasion Furnace

STATEX 125 ISAF Intermediate Super Abrasion Furnace



STATEX R HAF High Abrasion Furnace

STANDARD MICRONEX® MPC Medium Processing Channel



MICRONEX W-6 EPC Easy Processing Channel

STATEX B FF Fine Furnace

STATEX M FEF Fast Extruding Furnace

STATEX 93 HMF High Modulus Furnace

STATEX G GPF General Purpose Furnace



FURNEX® SRF Semi-Reinforcing Furnace

Plus our outstanding MAPICO
pure synthetic iron oxide pigments

REDS... 617, 297, 347, 387, 477 and 567

TANS... 10, 15 and 20

BROWNS... 418, 419, 420, 421 and 422

PLUS YELLOWS...



COLUMBIAN CARBON COMPANY

380 Madison Avenue, New York 17, N. Y.



DECEMBER • 1961

Volume XXXIV • Number Five

RUBBER CHEMISTRY
AND TECHNOLOGY

RUBBER REVIEWS

for 1961

PUBLISHED BY THE DIVISION
OF RUBBER CHEMISTRY OF THE
AMERICAN CHEMICAL SOCIETY



One stop shopping for Rubber Polymer values

Here, the customer is *always* right—when he chooses Philprene* rubber. Make Phillips your rubber shop-center. From tank tracks to intricate extrusions, there's a Philprene rubber for your special requirements. You can depend on prompt delivery. And you can depend on the valuable technical services offered by your Phillips representative.

* A trademark



PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Sales Div., 318 Water St., Akron 8, Ohio

Sales Offices: Akron, Chicago, Dallas, Providence and Trenton

West Coast: Harwick Standard Chemical Company, Los Angeles, California

Export Sales: Phillips Petroleum International Corporation, Sumatrastrasse 27, Zurich 6, Switzerland
Distributors of Phillips Chemical Company Products, 80 Broadway, New York 5, N. Y.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS, EXECUTIVE COMMITTEE AND LIBRARIAN

Chairman.....G. E. POPP, Phillips Chemical Company, Akron, O.
Vice-ChairmanG. H. SWART, General Tire & Rubber Co., Akron, O.
Secretary....L. H. HOWLAND, Naugatuck Chemical Division, Naugatuck, Conn.
Treasurer.....D. F. BEHNEY, Harwick Standard Chemical Co., Akron, O.
Assistant Treasurer.....GEORGE HACKIM, General Tire & Rubber Co., Akron, O.
Editor of *Rubber Chemistry and Technology*.....DAVID CRAIG, B. F. Goodrich
Research Center, Brecksville, O.

Advertising and Business Manager of *Rubber Chemistry and Technology*
GEORGE HACKIM, General Tire & Rubber Co., Akron, O.

Directors....W. S. COE (Past Chairman), A. W. SLOAN (Director-at-Large),
J. M. BOLT (Southern Rubber Group), G. W. SMITH (Boston), M.
H. LEONARD (Akron), C. V. LUNDBERG (New York), R. A. GARRETT
(Philadelphia), J. A. CARR (Canada), N. R. LEGGE (Northern Cali-
fornia), A. T. McPHERSON (Washington, D. C.), H. E. SCHWELLER
(Southern Ohio), M. J. O'CONNOR (Fort Wayne), H. D. SHETLER
(Chicago), R. H. SNYDER (Detroit), D. C. MADDY (Los Angeles),
J. FRANKFURTH (Buffalo), R. W. SZULIK (Rhode Island), R. T. ZIM-
MERMAN (Connecticut). *Alternate directors*: I. G. SJOTHUN (Akron),
W. F. MALCOLM (Boston), T. L. DAVIES (Canada), A. J. HAWKINS, JR.
(Los Angeles), J. T. DUNN (New York).

Councilors....W. S. COE.
(Alternates, C. S. YORAN, 1958-1960; J. D. D'IANNI).

Rubber Division Librarian....MRS. SANDRA GATES, Akron University, Akron, O.

COMMITTEES

Advisory Committee on Local Arrangements....C. A. SMITH, Chairman (New
Jersey Zinc Co., Cleveland, Ohio), S. L. BRAMS (Dayton Chemical
Products, West Alexandria, Ohio), W. H. PETERSON (Enjay Co.,
15 West 51 Street, New York City).

Auditing Committee....F. W. BURGER, Chairman (Phillips Chemical Co.,
Akron, Ohio), C. W. CHRISTENSEN (Monsanto Chemical Company,
Akron, Ohio), L. V. COOPER (Firestone Tire & Rubber Co., Akron,
Ohio).

Best Papers Committee....HAROLD TUCKER, *Chairman* (B. F. Goodrich Research Center, Brecksville, Ohio), H. E. HAXO (U. S. Rubber Company, Research Center, Wayne, N. J.), G. E. POPP (Phillips Chemical Company, Akron, Ohio).

Bibliography Committee....JOHN MCGAVACK, *Chairman* (144 Ames Avenue, Leonia, New Jersey), P. H. BIDDISON (Firestone Tire & Rubber Company, 352 Wayne Avenue, Akron, Ohio), V. L. BURGER (U. S. Rubber Company, Research Center, Wayne, New Jersey), LOIS BROCK (Research Laboratory, General Tire & Rubber Company, Akron, Ohio), D. E. CABLE (U. S. Rubber Company, Research Center, Wayne, New Jersey), H. E. HAXO (U. S. Rubber Company, Research Center, Wayne, New Jersey), MRS. JEANNE JOHNSON (U. S. Rubber Company, Research Center, Wayne, New Jersey), M. E. LERNER (*Rubber Age*, 101 West 31st Street, New York City), G. S. MILLS (U. S. Rubber Company, Research Center, Wayne, New Jersey), LEORA STRAKA (Goodyear Tire & Rubber Company, Akron, Ohio), MRS. M. L. RELYEA (36 Hopper Avenue, Pompton Plains, New Jersey), C. E. RHINES (U. S. Rubber Company, Research Center, Wayne, N. J.), D. F. BEHNEY (Harwick Standard Chemical Co., 60 S. Seiberling Street, Akron 5, Ohio).

By-Laws Revision Committee....G. ALLIGER, *Chairman* (Firestone Tire & Rubber Co., Akron, Ohio), W. C. WARNER (General Tire & Rubber Co., Akron, Ohio), R. A. GARRETT (Armstrong Cork Co., Lancaster, Pa.), L. H. HOWLAND (Naugatuck Chemical Division, Naugatuck, Conn.).

Editorial Board of Rubber Reviews....G. E. P. SMITH, JR. *Chairman* (Firestone Tire and Rubber Co., Akron, Ohio), J. REHNER, JR. (Esso Research & Engineering Co., Linden, N. J.), B. L. JOHNSON (Firestone Tire & Rubber Co., Akron, Ohio), S. D. GEHMAN (Goodyear Tire & Rubber Co., Akron, Ohio), D. CRAIG (B. F. Goodrich Research Center, Brecksville, Ohio), W. R. SMITH (The Cabot Corporation, Cambridge, Mass.).

Education Committee....C. V. LUNDBERG, *Chairman* (Bell Telephone Laboratories, Inc., Murray Hill, New Jersey), R. D. STIEHLER (National Bureau of Standards, Washington, D. C.), W. F. BUSSE (E. I. du Pont de Nemours & Co., Wilmington, Delaware), H. D. SHETLER (Chicago Rawhide Manufacturing Co., 1301 Elston Avenue, Chicago 22, Illinois), H. E. SCHWELLER (Inland Manufacturing Division, General Motors Corporation, Dayton 1, Ohio), R. A. GARRETT (Armstrong Cork Co., Lancaster, Pennsylvania), MILTON H. LEONARD (Columbian Carbon Company, Akron, Ohio).

Files & Records Committee....J. D. D'IANNI, *Chairman* (Goodyear Tire & Rubber Co., Akron, Ohio), DOROTHY HAMLEN (University of Akron, Akron, Ohio), E. A. WILLSON (B. F. Goodrich Research Center, Brecksville, Ohio).

Finance Budget Committee....L. V. COOPER, *Chairman* (Firestone Tire & Rubber Company, Akron, Ohio), C. W. CHRISTENSEN (Monsanto Chemical Company, Akron, Ohio), F. W. BURGER (Phillips Chemical Company,

Akron, Ohio), E. H. KRISMANN (E. I. du Pont de Nemours & Co., Akron, Ohio), S. B. KUYKENDALL (Firestone Tire & Rubber Co., Akron, Ohio), D. F. BEHNEY, *Ex-officio* (Harwick Standard Chemical Co., 60 S. Seiberling Street, Akron 5, Ohio).

Future Meetings.... A. E. LAURENCE, *Chairman* (R. T. Vanderbilt Co., Akron, Ohio), G. N. VACCA (Bell Telephone Laboratories, Murray Hill, N. J.), J. M. BOLT (Naugatuck Chemical Co., Olive Branch, Miss.).

Library Operating Committee.... GUIDO H. STEMPER, *Chairman* (The General Tire & Rubber Company, Central Research Laboratories, Akron 9, Ohio), MAURICE MORTON (University of Akron, Akron, Ohio), MRS. SANDRA GATES (University of Akron, Akron, Ohio), MISS DOROTHY HAMLEN (University of Akron, Akron, Ohio).

Library Policy Committee.... GUIDO H. STEMPER, *Chairman* (The General Tire & Rubber Co., Central Research Laboratories, Akron 9, Ohio), ROBERT L. BEBB (Firestone Tire & Rubber Company, Akron, Ohio), A. M. CLIFFORD (Goodyear Tire & Rubber Company, Akron, Ohio), MAURICE MORTON (University of Akron, Akron, Ohio), EARL C. GREGG, JR. (The B. F. Goodrich Company, Akron, Ohio), D. F. BEHNEY, *Ex-officio* (Harwick Standard Chemical Co., 60 S. Seiberling Street, Akron 5, Ohio).

Membership Committee.... MAURICE J. O'CONNOR, *Chairman* (O'Connor and Company, Inc., 4667 North Manor Avenue, Chicago 25, Illinois), All Directors from each Local Rubber Group, C. E. HUXLEY (Enjay Company, Inc., 130 East Randolph Drive, Chicago, Illinois), A. M. GESSLER (Esso Research & Engineering Company, Linden, New Jersey), E. M. DANNENBERG (Cabot Corporation, 38 Memorial Drive, Cambridge 42, Massachusetts).

New Publications Committee.... R. G. SEAMAN, *Chairman* (Rubber World, New York City), D. CRAIG (B. F. Goodrich Research Center, Brecksville, Ohio), J. M. BALL (Midwest Rubber Reclaiming Co., 95 Whipstick Road, Wilton, Conn.), G. E. P. SMITH, JR. (Firestone Tire & Rubber Co., Akron, Ohio).

Nomenclature Committee.... RALPH F. WOLF, *Chairman* (4448 Lahm Drive, Akron 19, Ohio), I. D. PATTERSON (Goodyear Tire & Rubber Co., Akron, Ohio), F. W. GAGE (Dayton Chemical Products Laboratories, W. Alexandria, Ohio), E. E. GRUBER (General Tire & Rubber Co., Akron, Ohio), A. T. MCPHERSON (National Bureau of Standards, Washington, D. C.), R. W. SZULIK (Acushnet Process Co., New Bedford, Mass.).

Nominating Committee.... LARRY M. BAKER, *Chairman* (General Tire & Rubber Company, Akron, Ohio), JAMES D. D'IANNI (The Goodyear Tire & Rubber Company, Akron 16, Ohio), KENNETH R. GARVICK (The Mansfield Tire & Rubber Company, P. O. Box 428, Mansfield, Ohio), ROBERT G. SEAMAN (Editor, *Rubber World*, 630 Third Avenue, New York 17, N. Y.), GEORGE VACCA (Bell Telephone Laboratories, Murray Hill, New Jersey).

Officers Manual... A. E. JUVE, *Chairman* (B. F. Goodrich Research Center, Brecksville, Ohio), B. S. GARVEY (Pennsalt Chemicals Corp., Philadelphia, Pa.).

Papers Review Committee... W. S. COE, *Chairman* (Naugatuck Chemical Division, U. S. Rubber Company, Naugatuck, Connecticut), W. J. SPARKS (Esso Research & Engineering Company, P. O. Box 51, Linden, New Jersey), DAVID CRAIG (Editor, RUBBER CHEMISTRY & TECHNOLOGY, B. F. Goodrich Research Center, Brecksville, Ohio), L. H. HOWLAND (Naugatuck Chemical Division, U. S. Rubber Company, Naugatuck, Connecticut), G. E. POPP (Phillips Chemical Company, Rubber Chemicals Sales Division, 318 Water Street, Akron 8, Ohio).

Program Planning Committee... GEORGE E. POPP, *Chairman* (Phillips Chemical Company, Rubber Chemicals Sales Division, 318 Water Street, Akron 8, Ohio), J. D. D'IANI (The Goodyear Tire & Rubber Co., Akron 8, Ohio), DAVID CRAIG (Editor, RUBBER CHEMISTRY & TECHNOLOGY, B. F. Goodrich Research Center, Brecksville, Ohio), MERTON STUDEBAKER (Phillips Chemical Company, 318 Water Street, Akron 8, Ohio), W. F. TULEY (Naugatuck Chemical Division, U. S. Rubber Company, Naugatuck, Connecticut).

Selection Committee for the Rubber Science Hall of Fame, University of Akron, representatives of the Division of Rubber Chemistry... A. E. JUVE (B. F. Goodrich Research Center, Brecksville, Ohio), RALPH F. WOLF (4448 Lahm Drive, Akron 19, Ohio).

Tellers... A. C. STEVENSON, *Chairman* (E. I. du Pont de Nemours & Co., Wilmington, Del.), L. T. EBY (Esso Research and Engineering Co., Elizabeth, N. J.), PAUL ROACH (Texas-U. S. Chemical Co., Parsippany, N. J.).

FUTURE MEETINGS

ACS MEETINGS AS OF SEPTEMBER 5, 1961

Meeting	Date	City
Spring 1962	March 20-29	Washington, D. C.
Fall 1962	Sept. 9-14	Atlantic City, N. J.
Jan. 1963	Experimental Third National Meeting	
Spring 1963	Mar. 31-Apr. 5	Los Angeles, Calif.
Fall 1963	Sept. 8-13	New York, N. Y.
Jan. 1964	Experimental Third National Meeting	
Spring 1964	Mar. 31-Apr. 9	Philadelphia, Pa.
Fall 1964	Aug. 30-Sept. 4	Chicago, Ill.
Spring 1965	Mar. 30-Apr. 9	Detroit, Mich.
Fall 1965	Sept. 12-17	Atlantic City, N. J.
Spring 1966	March 22-31	Pittsburgh, Pa.
Fall 1966	Sept. 11-16	New York, N. Y.
Spring 1967		
Fall 1967	Sept. 10-15	Chicago, Ill.
Spring 1968		
Fall 1968	Sept. 8-13 (T)	Atlantic City, N. J.

(T) Tentative.

RUBBER DIVISION MEETINGS

	Date	City	Hdqtr. Hotel	Exh. Space
Spring 1962	Apr. 24-27	Boston, Mass.	Statler	—
Fall 1962	Oct. 16-19	Cleveland, O.	Sheraton	Maybe
Spring 1963	May 7-10	Toronto, Canada	Royal York	Yes
Fall 1963	Sept. 10-13	New York, N. Y.	Roosevelt	Maybe
Spring 1964	Apr. 28-May 1	Detroit, Mich.	Cadillac	Yes
Fall 1964	Sept. 1-4	Chicago, Ill.	Sherman	Yes
Spring 1965	May 4-7	Miami Beach, Fla.	Fontainebleau	Yes
Fall 1965	Oct. 19-22	Philadelphia, Pa.	Bellevue-Strat	
Spring 1966	May 3-6	San Francisco, Cal.	Fairmount	Yes
Fall 1966	Sept. 13-16	New York, N. Y.	Roosevelt ¹	
Spring 1967	May 2-5	Montreal, Canada	Queen Elizabeth	Yes
Fall 1967	Sept. 12-15	Chicago, Ill.	Sherman	Yes

SPONSORED RUBBER GROUPS OFFICERS AND MEETING DATES

1961

AKRON RUBBER GROUP INC.

Chairman: J. H. GIFFORD (Witco Chemical, 213 W. Bowery St., Akron, Ohio). *Vice-Chairman:* R. B. KNILL (Goodyear Tire & Rubber, Akron, Ohio). *Secretary:* B. N. LARSEN (Naugatuck Chemical, 9 Overwood Road, Akron 13, Ohio). *Treasurer:* BEN KASTEIN (Firestone Tire & Rubber, 1200 Firestone Parkway, Akron, Ohio). *Area Director:* M. H. LEONARD (Columbian Carbon, 452 E. Market St., Akron, Ohio). *Past Chairman:* I. J. SJOTHUN (Firestone Tire & Rubber, 1200 Firestone Parkway, Akron, Ohio). *Program:* A. E. LAURENCE (2425 Amesbury Road, Akron, Ohio). *Publicity:* RALPH F. ANDERSON (B. F. Goodrich Company, 500 S. Main St., Akron, Ohio). *Tickets:* R. J. BROWN (Goodyear Tire & Rubber, 1144 E. Market St., Akron, Ohio). *Membership:* D. M. STRASSER (Witco Chemical, 213 W. Bowery St., Akron, Ohio). *Meeting dates for the 1961-62 Season:* Sheraton Hotel (meeting) Friday October 20, 1961; Sheraton Hotel (meeting) Friday January 26, 1962; Sheraton Hotel (dance) Friday February 23, 1962; Sheraton Hotel (meeting) Thursday April 5, 1962; outing, Firestone Country Club Friday June 22, 1962. *Meeting dates for 1962-1963 Season:* Sheraton Hotel (meeting) Friday October 26, 1962; Sheraton Hotel (meeting) Friday January 25, 1963; Sheraton Hotel (Dance) Friday February 22, 1963; Sheraton Hotel (meeting) Thursday April 4, 1963. *Outing:* Firestone Country Club Friday June 21, 1963.

BOSTON RUBBER GROUP

Chairman: GEORGE E. HERBERT (Tyer Rubber Company, Andover, Massachusetts). *Vice-Chairman:* JOHN M. HUSSEY (Goodyear Chemical Company, Needham Heights 94, Massachusetts). *Secretary-Treasurer:* GEORGE H. HUNT (Simplex Wire & Cable Company, Cambridge 39, Massachusetts). *Executive Committee:* JAMES J. BREEN (Barrett & Breen Co., Boston 10, Massachusetts). *CHESTER STOEKELS* (Firestone Tire & Rubber Company, Fall River, Massachu-

¹ Tentative.

setts). ROBERT LOVELAND (R. T. Vanderbilt Company, Boston, Massachusetts). GEORGE W. SMITH (E. I. du Pont de Nemours & Co., Boston, Massachusetts). *Officers Tenure*: January 1, 1961-January 1, 1962. *Meeting Dates*: (1961)—February 3, 4, 5; March 17; June 16; October 13; and December 15.

BUFFALO RUBBER GROUP

Chairman: E. F. SVERDRUP (U. S. Rubber Reclaiming Company, Buffalo 5, New York). *Vice-Chairman*: E. R. MARTIN (Dunlop Tire and Rubber Corporation, Buffalo 5, New York). *Secretary-Treasurer*: E. J. HAAS (Dunlop Tire and Rubber Corporation, Buffalo 5, New York). *Asst. Secretary-Treasurer*: R. J. O'BRIEN (Dunlop Tire and Rubber Corporation, Buffalo 5, New York). *Directors*: D. SCHULER, C. PEPPER, J. FRANKFURTH, R. LINDBERG, S. MURRAY, F. O'CONNOR. *Officers Tenure*: December 1960-December 1961. *Director to Div. of Rubber Chemistry*: J. FRANKFURTH. *Meeting Dates*: March 7, May 12, June 13, October 10 and December 12.

CHICAGO RUBBER GROUP, INC.

President: THEODORE C. ARGUE (Roth Rubber Company, Cicero, Illinois). *Vice-President*: ROBERT KANN (Goodyear Chemical Division, Elk Grove, Illinois). *Secretary*: HAROLD STARK (2247 S. 17th Avenue, Broadview, Illinois). *Treasurer*: STANLEY D. SHAW (Witco Chemical Company, Chicago, Illinois). *Directors*: FRED KLEPETAR (Johns-Manville Corporation, Chicago, Illinois). JOSEPH E. STONIS (The C. P. Hall Company, Chicago, Illinois). CHARLES F. WIMMER (Phillips Chemical Company, Elmhurst, Illinois). CORNELIUS WOODS (514 Wenonah Avenue, Oak Park, Illinois). JAMES DUNNE (United Carbon Company, Inc., La Grange, Illinois). BATEMAN G. HUTCHISON (Copolymer Rubber & Chem. Co., Homewood, Illinois). AL D. MARR (Judson Rubber Works, Chicago, Illinois). HAROLD D. SHETLER (Chicago Rawhide Mfg. Co., Chicago, Illinois). *Legal Counsel & Executive Secretary*: EDWARD H. LEAHY (333 N. Michigan Ave., Chicago, Illinois). *Meeting dates for the 1961-1962 season*: September 29, November 17, 1961; January 26, March 16 and May 4, 1962. The meetings are at the Furniture Club except for the Christmas Party, Dec. 15 at the Morrison Hotel.

CONNECTICUT RUBBER GROUP

Chairman: FRANK B. SMITH (Naugatuck Chemical Company, Naugatuck, Connecticut). *Vice-Chairman*: ALEXANDER MURDOCK, JR. (Armstrong Rubber Company, West Haven, Connecticut). *Secretary*: RIAL S. POTTES, JR. (Spencer Rubber Products, Manchester, Connecticut). *Treasurer*: FRANK F. VILLA (Whitney Blake Company, Hamden, Connecticut). *Directors*: VINCENT P. CHADWICK, FRANCIS H. H. BROWNING, KEN C. CROUSE, RICHARD STIMETS, CARL LAWSON. *Director to Division of Rubber Chemistry*: R. T. ZIMMERMAN. *Meeting Dates*: February 17, May 19, September 9 and November 17. *Officers Tenure*: January 1, 1961 to January 1, 1962.

DETROIT RUBBER AND PLASTICS GROUP

Chairman: W. D. WILSON (R. T. Vanderbilt Company, 5272 Doherty Dr., Orchard Lake, Michigan). *Vice-Chairman*: S. M. SIDWELL (Chrysler Engineering Division, P. O. Box 1118, Dept. 821, Detroit 21, Michigan). *Treasurer*: P. V. MILLARD (Automotive Rubber Company, 12550 Beech Road, Detroit 39,

Michigan). *Secretary*: R. W. MALCOLMSON (E. I. du Pont de Nemours & Company, 13000 W. Seven Mile Road, Detroit 35, Michigan). *Executive Committee*: W. F. MILLER, E. J. KVET, H. W. HOERAUF, C. H. ALBERS, C. E. BECK, E. I. BOSWORTH, R. C. CHILTON, F. G. FALVEY, E. P. FRANCIS, T. W. HALLORAN, J. F. MASDEN, J. M. McCLELLAN, R. H. SNYDER, R. C. WATERS, P. WEISS. *Officers Tenure*: December 1959–December 1960. *Director to Div. of Rub. Chem., ACS*: R. H. SNYDER (to 1962). *Meeting Dates*: (1961)—Feb. 17, Apr. 21, June 23, Oct. 5 and December 8.

FORT WAYNE RUBBER & PLASTICS GROUP

Chairman: A. L. ROBINSON (Harwick Standard Chemical Company, 2724 West Lawrence Avenue, Chicago 25, Illinois). *Vice-Chairman*: CARROLL VOSS (General Tire & Rubber Company, Wabash, Indiana). *Secretary-Treasurer*: ROBERT O. HARTMAN (Monsanto Chemical Company, Chicago, Illinois). *Directors*: A. G. COBBE, GERARD ZWICK, B. G. HUTCHINSON, JOHN WALSH, CARROLL HOBSON, JACK LIPPINCOTT, BALFOUR CONNELL, ROBERT WADE. *Meeting Dates* for 1961–1962 at Van Orman Hotel Ft. Wayne, Indiana: September 28, December 7, February 8, April 5. *Summer Outing* June 8, 1962 Tippecanoe Country Club Leesburgh, Indiana: September 20, December 6, February 7, April 18, 1963. *Summer Outing* June 7, 1963.

LOS ANGELES RUBBER GROUP, INC.

Chairman: W. M. ANDERSON (Gross Manufacturing Co., Inc., 1711 S. California Avenue, Monrovia, California). *Assoc. Chairman*: C. M. CHURCHILL (Naugatuck Chemical Division, U. S. Rubber Company, 5901 Telegraph Rd., Los Angeles 22, California). *Vice-Chairman*: L. W. CHAFFEE (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Treasurer*: J. L. RYAN (Shell Chemical Company, P. O. Box 6066, Lakewood, California). *Secretary*: C. F. ASHCROFT (Cabot Corporation, 3350 Wilshire Blvd. #718, Los Angeles 5, California). *Directors*: DON MONTGOMERY (1961–1962), HOWARD R. FISHER (1961–1962), L. E. PETERSON (1961–1962), R. L. WELLS (1960–1961), HAROLD W. SEARS (1960–1961), HAROLD J. BRANDENBURG (1960–1961), B. R. SNYDER (1961). *Asst. Treasurer*: ROBERT F. DOUGHERTY (U. S. Rubber Company, 5675 Telegraph Rd., Los Angeles 22, California). *Asst. Secretary*: W. C. SCHEUERMANN (Plastic & Rubber Products Co., 2100 Hyde Park Blvd., Los Angeles 47, California). *Historian & Librarian*: ROY N. PHELAN (Atlas Sponge Rubber Co., 1707 S. California Avenue, Monrovia, California). *Attorney*: CECIL COLLINS (2875 Glendale Blvd., Los Angeles 39, California). *Photographer Emeritus*: L. E. BUDNICK (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Official Photographer*: BERT SLUYTER (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Director to Division of Rubber Chemistry*: D. C. MADDY (to 1963), (Harwick Standard Chemical Company, 7225 Paramount Blvd., Pico Rivera, California). *Officers Tenure*: December, 1960 to December, 1961. *Meeting Dates*: (1961)—February 7, March 7, April 4, May 2, October 3 and November 7.

NEW YORK RUBBER GROUP

Chairman: R. DETURK (Cooke Color & Chemical Co., Hackettstown, N. J.). *Vice-Chairman*: A. H. WOODWARD (E. I. du Pont de Nemours & Co., Trenton, N. J.). *Sgt. at Arms*: FRANK RABA. *Secretary-Treasurer*: M. E. LERNER

(Rubber Age, 101 West 31st St., N. Y., N. Y.). *Directors:* J. T. DUNN, M. A. DURAKIS, W. R. HARTMAN, J. E. WALSH, R. T. AMBROSE, W. C. CARTER, A. M. GESSLER, J. V. FUSCO, G. C. VICKERY, W. F. WADE, G. G. WINSPEAR. *Ex-officio Members:* H. J. PETERS, R. S. WALKER. *Officers Tenure:* January 1, 1961–January 1, 1962. *Director to Div. of Rub. Chem., ACS:* C. V. LUNDBERG (to 1963). *Meeting Dates:* (1961)—Mar. 24, June (Summer Outing), Aug. 1, Oct. 20 and Dec. 15. (1962)—Mar. 23, June 7, Aug. (Golf Outing), Oct. 19 and Dec. 14.

NORTHERN CALIFORNIA RUBBER GROUP

Chairman: VIRGIL C. PRICE (Burke Rubber Company, 2250 South Tenth Street, San Jose 3, California). *Vice-Chairman:* VICTOR J. CARRIERE (Mansfield Tire & Rubber Company, 4901 East 12th Street, Oakland, California). *Treasurer:* GENE L. UNTERZUBER (Oliver Tire & Rubber Company, 1256 65th Street, Oakland 8, California). *Secretary:* ROGER H. THATCHER (Union Rubber Company, 1002 77th Avenue, Oakland 21, California). *Directors:* EUGENE GADOR, HENRI KRAKOWSKI, ROBERT B. STEWART. *Officers Tenure:* December, 1960–December, 1961. *Meeting Dates:* January 12, February 9, March 9, April 13, May 11, June 8, September—open date for Summer Outing, October 12, November 9, December—open for Christmas Party.

THE PHILADELPHIA RUBBER GROUP

Chairman: R. N. HENDRIKSEN (Phillips Chemical Company, Trenton, New Jersey). *Vice-Chairman:* R. M. KEER (H. K. Porter Company, Thermoid Division, Philadelphia, Pa.). *Secretary-Treasurer:* H. F. SMITH (Naugatuck Chemical Company, 97 Bayard Street, New Brunswick, New Jersey). *Historian:* J. B. JOHNSON (Linear, Inc., Philadelphia, Pa.). *Executive Committee:* E. C. BROWN, K. E. CHESTER, R. E. CONNOR, W. J. MACOMBER, K. F. QUINN, B. VAN ARKEL. *Director to Division of Rubber Chemistry:* R. A. GARRETT (to 1962). *Officers Tenure:* January 1, 1961 to January 1, 1962. *Meeting Dates:* January 27, April 28, August 18, October 13, November 3.

RHODE ISLAND RUBBER GROUP

Chairman: E. C. UHLIG (U. S. Rubber Co., Providence). *Vice-Chairman:* J. M. VITALE (The Crescent Wire Company, Inc., Pawtucket, Rhode Island). *Secretary-Treasurer:* C. A. DAMICONE (Acushnet Process Co., New Bedford, Massachusetts). *Directors:* J. M. DONAHUE, P. HASTINGS, V. CASEY, T. CROSBY, F. CATALFANO. *Dir. Rubber Div. ACS:* R. SZULIK. *Permanent Historian:* ROBERT VAN AMBURGH. The officers tenure is from January 1, 1962 to January 1, 1963. The meeting dates are: April 5, June 7, and November 8, 1962.

SOUTHERN OHIO RUBBER GROUP

President: HOWARD G. GILLETTE (Precision Rubber Prod. Corp., Dayton, Ohio). *Vice-President:* E. N. IPIOTIS (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Secretary:* JOHN H. WOODWARD (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Treasurer:* DONALD R. STRACK (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Directors:* F. W. GAGE, HAROLD SCHWELLER, D. L. ALLEN, C. BELLANCA, R. HEIST, R. L. JACOBS, M. K. COULTER, J. WEST, H. S. KARCH, W. F. HERBERG, J. M. WILLIAMS. *Director to Division of Rubber Chemistry:*

H. E. SCHWELLER (1962). *Officers Tenure*: January 1, 1961–January 1, 1962.
Meeting Dates: March 23, June 3, September 28 and Dec. 9.

SOUTHERN RUBBER GROUP

Chairman: R. C. WHITMORE (Better Monkey Grip Company, P. O. Box 6170, Dallas 22, Texas). *Vice-Chairman*: C. M. WHITE (Cabot Carbon Company, 1309 Main St., Dallas 2, Texas). *Secretary*: R. W. RICE (Firestone Synthetic Rubber & Latex Co., Box 1361, Lake Charles, Louisiana). *Treasurer*: A. B. CRAIG, JR. (Witco Chemical Company, P. O. Box 22443, Houston, Texas). *Meeting Dates* are as follows: Nov. 17–18, 1961, Memphis, Tenn. (Chisca Hotel). Jan. 26–27, 1962, Houston, Texas (Shamrock-Hilton). June 8–9, 1962, Birmingham, Ala. (Dinkler-Tutwiler). Nov. 9–10, 1962, New Orleans, La. (Roosevelt).

WASHINGTON RUBBER GROUP

President: PHILIP MITTON (Materials Branch, U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia). *Vice-President*: THOMAS A. THARP (General Tire & Rubber Company, 1120 Conn. Avenue, N. W., Washington, D. C.). *Secretary*: DANIEL PRATT (Code 634 C, Bureau of Ships, Navy Department, Washington 25, D. C.). *Treasurer*: GEORGE G. RICHEY (National Bureau of Standards, Washington 25, D. C.). *Director of Division of Rubber Chemistry*: A. T. McPHERSON (to 1961). *Officers Tenure*: July 1, 1960 to July 1, 1961. *Meeting Dates*: January 25, March 8, April 19, May 17.

THE CHEMICAL INSTITUTE OF CANADA RUBBER DIVISION OFFICERS AND SPONSORED RUBBER GROUPS

Chairman: D. W. HAY (Polymer Corporation Limited, Sarnia, Ontario). *Vice-Chairman*: C. M. CROAKMAN (Columbian Carbon of Canada, Toronto, Ontario). *Secretary-Treasurer*: W. A. CLINE (Canadian General Tower Ltd., Galt, Ontario). *Directors*: A. HOLDEN (Canada Colors & Chemicals, Montreal, Quebec). W. J. NICHOL (Dunlop Canada Limited, Toronto, Ontario). L. ROBINSON (Canada Wire & Cable Co., Toronto, Ontario).

THE ONTARIO RUBBER GROUP

Chairman: W. R. SMITH (Dominion Rubber Company Ltd., Kitchener, Ontario). *Vice-Chairman*: L. V. LOMAS (c/o L. V. Lomas Chemical Company, Toronto, Ontario). *Secretary*: BRUCE WILLIAMS (Feather Industries Ltd., Toronto, Ontario). *Treasurer*: W. J. HOGG (Naugatuck Chemicals Division, Dominion Rubber Co., Ltd., Elmira, Ontario). *Membership Chairman*: FRANK CAPSTICK (Dunlop Canada Ltd., Toronto, Ontario). *Entertainment Chairman*: B. AUSTIN (Firestone Tire & Rubber Co., Hamilton, Ontario).

QUEBEC RUBBER & PLASTICS GROUP

Chairman: E. W. MAY (Naugatuck Chemicals, P. O. Box 130, Place d'Armes, Montreal, Quebec). *Past & Vice Chairman*: J. M. CAMPBELL (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Secretary*: L. V. WOYTIUK (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Treasurer*: R. B. PILMER (Dominion

Rubber Co. Ltd., P. O. Box 130, Place d'Armes, Montreal, Quebec). *Membership*: E. T. CHALLACOMBE (Du Pont of Canada Ltd., P. O. Box 660, Montreal, Quebec). *Fall Smoker*: D. B. GUSTARD (Columbian Carbon (Canada) Ltd., Carbon Black and Pigment Division, 7147 Park Ave., Montreal 15, Quebec). *Golf Outing*: R. M. BLACK (Bate Chemical Corporation, 470 Bridge St., Montreal, Quebec). *Publicity*: R. R. VINCENT (Dominion Rubber Co. Ltd., P. O. Box 130, Place d'Armes, Montreal, Quebec). *Education*: DR. F. R. MOREHOUSE (Shawinigan Chemicals Ltd., Development Department, 600 Dorchester St. West, Montreal, Quebec). *Speakers*: J. A. NEAL (H. L. Blachford Ltd., 977 Aqueduct Street, Montreal, Quebec). *House Committee*: R. W. DICKSON (The Pigment and Chemical Co. Ltd., 6333 Decarie Blvd., Montreal 29, Quebec). *Ladies Night*: L. B. DUNFORD (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Sgt. at Arms*: J. R. CLOUTIER (Northern Electric Co. Ltd., Wire and Cable Division, P. O. Box 6122, Montreal, Quebec). *Director at Large*: A. R. OVERING (British Rubber Co. Ltd., 500—20th Ave., Lachine, Quebec).

ELECTION RESULTS—1961

DIVISION OF RUBBER CHEMISTRY, ACS

Officers (One-Year Term)

Chairman	G. E. Popp
Vice-Chairman	G. H. Swart
Secretary	L. H. Howland
Treasurer	D. F. Behney
Director-at-Large	A. W. Sloan

Directors and Alternates—Rubber Group Areas

(Three-Year Term)

Chicago	A. L. Robinson	Director
	A. G. Cobbe	Alternate
Connecticut	H. Gordon	Director
	B. Y. Connell	Director
Fort Wayne	R. L. Blair	Alternate
	J. M. Bolt	Director
Southern Rubber	A. B. Craig, Jr.	Alternate
	L. A. Wood	Director
Washington	J. R. Britt	Alternate

THE BIOSYNTHESIS OF RUBBER

P. FOURNIER AND TUONG-CHI-CUONG

INSTITUT FRANCOIS DU CAOUTCHOUC, PARIS, FRANCE

CONTENTS

	PAGE
Introduction.....	1230
I. Generalities concerning the biosynthesis of <i>cis</i> -polyisoprene.....	1231
II. Biosynthesis of <i>cis</i> -polyisoprene in the plant.....	1233
A. Anatomy of the tissues of <i>hevea brasiliensis</i> and its relationship to the production of rubber.....	1233
B. The laticiferous cell: its organization and functions.....	1235
1. General description of a cell.....	1235
2. Cellular metabolism.....	1236
3. The laticiferous cell and the biosynthesis of polyisoprene.....	1240
III. The first approaches to the problem of the biosynthesis of rubber.....	1243
A. The theories prior to 1950.....	1244
B. The work of Bonner and coworkers (1950).....	1247
C. Studies leading to doubtful conclusions.....	1249
D. Conclusions.....	1252
IV. The biosynthesis of terpenes.....	1253
A. Formation of the branched structure.....	1253
1. Formation of acetyl coenzyme A.....	1253
a. Formation of acetyl coenzyme A by glycolysis.....	1253
b. Formation of acetyl coenzyme A by β -oxydation of fatty acids.....	1258
2. Formation of acetoacetyl coenzyme A.....	1261
3. Formation of β -hydroxy β -methyl glutaryl coenzyme A.....	1263
a. Condensation of acetyl coenzyme A with acetoacetyl coenzyme A.....	1263
b. Degradation of leucine.....	1265
B. Formation of "active isoprene".....	1270
1. Formation of mevalonic acid.....	1270
2. Formation of 5-phosphomevalonic acid and pyrophosphomevalonic acid.....	1274
3. Formation of isopentenyl pyrophosphate.....	1277
C. Initiation.....	1278
D. Condensation of isoprene units.....	1280
1. Head-to-tail condensation mechanism.....	1280
a. Formation of geranyl pyrophosphate.....	1280
b. Formation of farnesyl pyrophosphate.....	1282
c. Subsequent head-to-tail condensation of farnesyl pyrophosphate.....	1283
2. Tail-to-tail condensation mechanism.....	1283
E. Termination.....	1286
F. Control and regulation of the metabolism of terpenes.....	1286

V. Biosynthesis of <i>cis</i> -polyisoprene, a special type of terpene.....	1287
A. Evidence for the function of acetic acid.....	1288
B. Evidence for the function of β -methylcrotonic acid.....	1294
C. Evidence for the function of mevalonic acid.....	1295
D. Evidence for the function of isopentenyl pyrophosphate.....	1298
E. Conclusions.....	1299
VI. Physiology of <i>hevea brasiliensis</i> and biosynthesis of <i>cis</i> -polyisoprene.....	1299
VII. Conclusions.....	1303
VIII. References.....	1303

INTRODUCTION

The importance of recent advances in biology is obvious, particularly in its influence upon medicine. Thus, the knowledge of the mechanism of cellular functions puts chemotherapy on a less empirical basis.

Research in this field has reached the point where practical applications become possible and where theoretical results can be transposed into practice.

In plant physiology, that is, the study of exchanges within plants, the same trends appear and many laboratories are occupied with the study of possible improvements in various plant syntheses. Theoretical research done on the biogenesis of terpenes has captured the attention of most laboratories specializing in the study of natural rubber where there is interest in possible applications.

Certain techniques concerned with physiological diagnosis are used successfully in the improvement of yield but since they do not explain the theoretical mechanism involved their applications are limited and leave the researcher helpless in cases which often escape empirical rules.

It is known that 75% of the production of a monoclonal lot is contributed by 25% of the trees. This means, that in spite of similar production conditions, great differences exist between yields of individual trees. Only the study of phenomena determining the formation of *cis*-polyisoprene will reveal the origin of such differences.

Today, this is certainly one of the most challenging problems put before researchers, because it touches directly upon plant life, each aspect of which bears some influence upon the problem to be studied. Therefore, research has become more complex, attempts to correlate and summarize acquired knowledge have become more difficult as various branches of science are required to classify and correlate the information. For example, it is not possible to describe the chemical reactions leading to polyisoprene without mentioning either the organization of the laticiferous cell which produces it, or the basic work done with other terpenes. This has brought us to summarize briefly certain information relative to the constitution of the plant cell and to enzymology in order to refresh the memory of those readers not familiar with these fields and to present to them the main points and the corresponding vocabulary.

To give an outline of cellular biology is a risky endeavor. Statements made too short for the sake of brevity in order to avoid overloading the text do not convey the complexity of the problem and the impressions obtained therefrom may be erroneous.

Before analyzing the knowledge acquired up to now, it should be mentioned that Bonner and Galston¹, in a remarkable monograph published in 1947, have been first to summarize the work done on the cellular biosynthesis of rubber. This literature study has served as a basis for much later research work and

Bonner can be considered to be one of the contributing forces to its present success.

It should also be mentioned that the study of the biosynthesis of terpenes, of which *cis*-polyisoprene is a representative, has known a development without precedent since the discovery in 1956 of one of its specific intermediates: mevalonic acid.

This discovery, together with the broad utilization of radioactive carbon C¹⁴ since 1945, has made it possible within a few years to explain one of the most interesting mechanisms in biology. The evolution of technique has rendered obsolete many contributions valuable at first but the sensitivity of newer methods makes possible a number of observations previously out of reach. Speculation has been replaced by experimental evaluation.

LIST OF ABBREVIATIONS

RNA	Ribonucleic acid
DNA	Desoxyribonucleic acid
ATP	Adenosine triphosphate
ADP	Adenosine diphosphate
AMP	Adenosine monophosphate
DPN, DPNH ₂	Diphosphopyridine nucleotide, oxidized or reduced
TPN, TPNH ₂	Triphosphopyridine nucleotide, oxidized or reduced
FAD, FADH ₂ , or F, FH ₂	Flavine adenine dinucleotide, oxidized or reduced
DPT	Diphosphothiamine
CoA, CoA-SH	Coenzyme A
P _{min}	Phosphate ion
PP _{min}	Pyrophosphoric ion
IPP or IsPP	Isopentenyl pyrophosphate
Dmal PP	Dimethylallyl pyrophosphate
Ge PP	Geranyl pyrophosphate
Fa PP	Farnesyl pyrophosphate
BMC	β -Methylcrotonic acid
HIV	β -Hydroxyisovaleric acid
HMG	β -Hydroxy- β -methylglutaric acid
IVA	Isovaleric acid
MG	β -Methylglutaconic acid
MVA	Mevalonic acid
MVAL	Mevaldic acid
5 P MVA	5-Phosphomevalonic acid
5 PP MVA	5-Pyrophosphomevalonic acid

I. GENERALITIES CONCERNING THE BIOSYNTHESIS OF *cis*-POLYISOPRENE

The purpose of this section is to summarize schematically the sequence of reactions which lead to *cis*-polyisoprene, thus serving as reference to the reader of the following sections. The basis for the present summary will follow in section IV.

The laticiferous cell is fed by a solution rich in glucides, supplied either by the leaves or by the neighbor cells rich in hemicellulosic reserves. The glucides (carbohydrates) serve as the main source of carbon in the formation of *cis*-polyisoprene.

In a first phase, called *glycolysis*, the glucides are transformed into acetic acid. This reaction is of a very generalized nature and takes place in most living cells. The acetic acid thus formed condenses with itself to form acetoacetic acid and the addition of a third molecule of acetic acid produces β -hydroxy- β -methyl glutaric acid (HMG) (Figure 1a).

One of the carboxyl groups of HMG acid is reduced to a hydroxyl group and the resulting compound is called mevalonic acid (MVA). The newly created hydroxyl group will give a pyrophosphoric ester. The remaining carboxyl group is eliminated simultaneously with the hydroxyl group in the β -position. The isopentenyl pyrophosphate (IsPP) resulting from this last reaction isomerizes in part to dimethylallyl pyrophosphate (DMAPP). The latter acts as an initiator and the polycondensation of these two compounds with elimination of pyrophosphoric acid to give *cis*-polyisoprene.

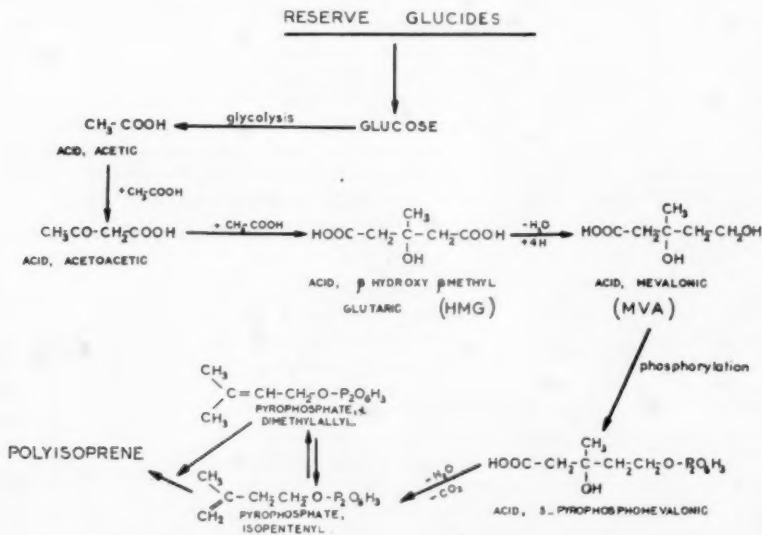


FIG. 1a.—Biosynthesis of polyisoprene. Reserve glucides means carbohydrate pool.

Presented in this manner, the biosynthesis of polyisoprene appears to be straightforward, resulting from a series of simple reactions according to the rules of organic chemistry. This apparent simplicity shows neither the difficulties one would encounter in reproducing those reactions by classical methods in the laboratory, nor the mediocre yields to be expected. Because, inside of the laticiferous cell, powerful organic catalysts go to work each individual transformation step is determined by the law of mass action. This selectivity makes any secondary reaction impossible, while in classical chemistry the contrary is often the common rule. It is believed, that the enzymes are localized in the living cell. This will bring us to summarize in a later section our knowledge relative to this subject.

This first analysis of the synthesis of *cis*-polyisoprene does not explain how

the energy necessary to such reactions is produced within the cell. As an example, the simple reaction (Figure 1b):

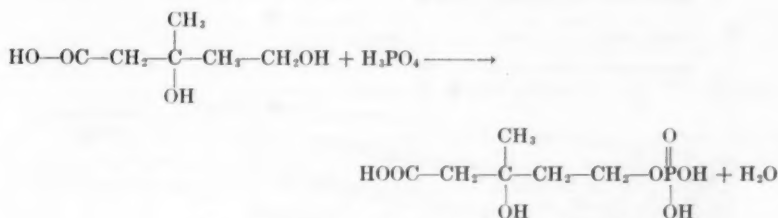


FIG. 1b.—Formation of 5-phosphomevalonic acid.

requires an energy of the order of 8 kcal/mole. Since this reaction is carried out under normal pressure and temperature, it is evident that this energy has to come from a certain source. Here again, the cellular mechanism providing the transmitting the energy will have to be described in a later section.

II. BIOSYNTHESIS OF *cis*-POLYISOPRENE IN THE PLANT

We would like to recall in this section some basic facts of plant anatomy and physiology necessary to recognize the role played by the living plant in the biosynthesis of *cis*-polyisoprene.

The hevea tree is not the only plant to produce rubber. A great number of plant species and even certain fungi² produce this substance, either in laticiferous vessels or in individual cells. But in most cases the rubber content is too low as to make any industrial recovery worth while. In all tropical zones the hevea tree is established as the cultivated rubber plant because of its high yield, ease of harvesting and because of the high quality of rubber produced.

A. ANATOMY OF THE TISSUES OF *HEVEA BRASILIENSIS* AND ITS RELATIONSHIP TO THE PRODUCTION OF RUBBER^{3,4}

The laticiferous tissues of hevea are located in all the soft tissues, that is in the leaves, flowers, seeds and in the bark of the branches, roots and stem. It is the stem which presents the greatest interest, because the laticiferous tissues are most abundant and most readily accessible to tapping.

As for all dicotyledons angiosperms, vascular phanerogams, the stem is composed of wood surrounded by bark. Bark and wood are separated by the cambium, a thin zone generating wood tissues towards the inside and bark tissues towards the outside. The inside parts of the bark contain soft bast tissues covered by cortical parenchyma sclerenchyma and the epiderm (Figure 2a).

The laticiferous vessels of hevea are part of the bast into which they are incorporated. They appear in the midst of the fibers, the soft bast cells and the sieve tubes. It is known that the latter ensure the circulation of the elaborated sap, that is the sap containing the carbohydrates produced by photosynthesis (Figure 2b). The crude sap is composed of water and mineral salts and flows through the wood vessels from bottom to top of the plant.

The laticiferous tissues follow the tissues of the bast in their development and their migration toward the interior as the cambium produces younger zones.

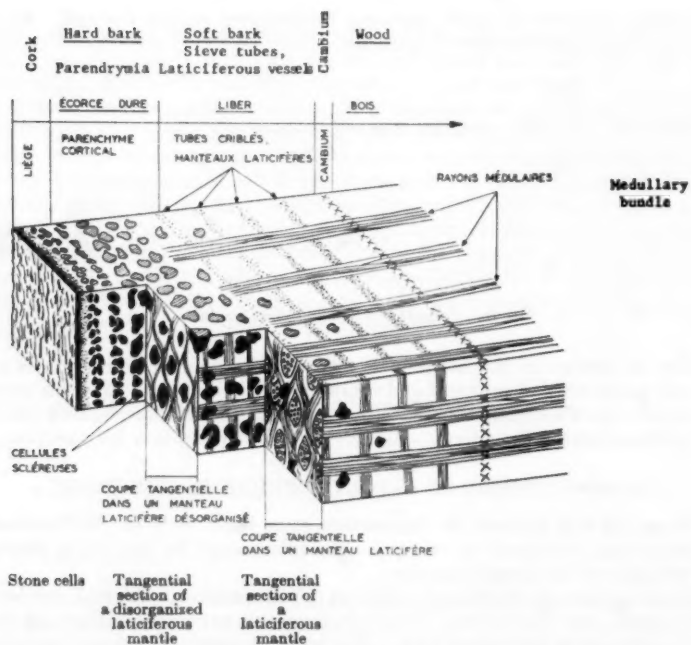


FIG. 2a.—Schematic section of bast formations.

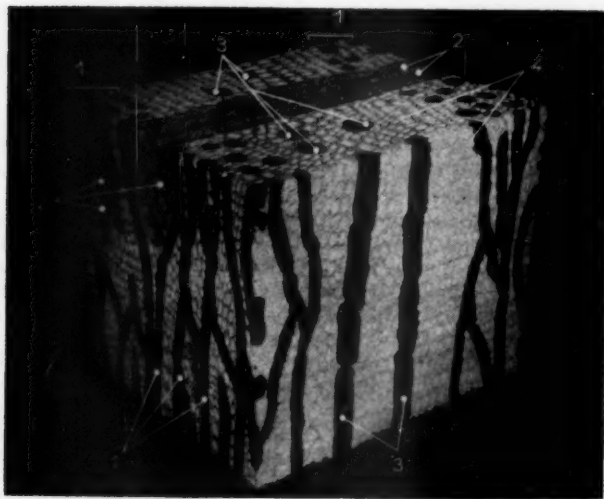


FIG. 2b.—Reconstitution of a bast section near the cambium. 1. Laticiferous vessels. 2. Medullary channels. 3. Sieve tubes. 4. Bast cells.

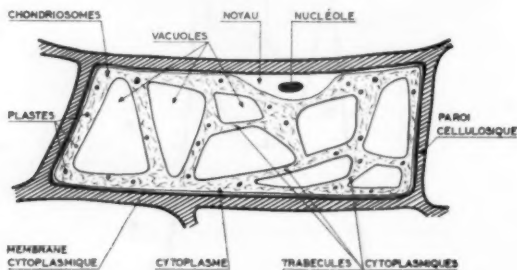
liquid or semiliquid, transparent substance called a lipo-proteidic hydrogel. The cytoplasm includes:

- a. hydrophylic sections or *vacuoles*, which are considered to be physiologically inert.
- b. the active elements of the cell:

The chondriome.

The particles contained in the cytoplasm of young cells are given the generic name of chondriosomes and together form the chondriome. The chondriomes appear under various forms:

straight fibers }	chondriontes
branched fibers }	mitochondrias
granules	chondriomites
granules in chains	



SCHEMA D'UNE CELLULE VÉGÉTALE ADULTE

Fig. 2d.—Schematic representation of an adult plant cell. *Paroi cellulosique* means cellulosic wall, *noyau* nucleus, *vacuole* vacuole, *nucléole* nucleolus and *trabecules* trabeculas.

With the mitochondrias should be associated a type of particle visible only by the electron microscope: the microsomes.

The plastidome.

In the adult cell, certain chondriosomes may change slowly into plastids, i.e., more voluminous organites which produce chlorophyll (chloroplastids), starch (amyloplastids or leucoplastids) or colored pigments (chromoplastids). The group of plastids forms the plastidome.

The nucleus.

The nucleus varies in shape, depending on the type of cell it belongs to. A so called nuclear membrane separates the nucleus from the cytoplasm.

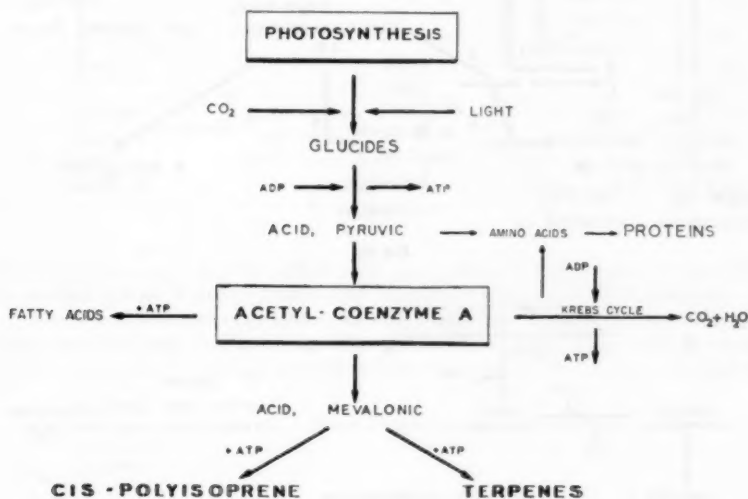
2. Cellular metabolism

The great majority of metabolic transformations taking place in the cells are determined by the action of enzymes, which are soluble, colloidal organic

catalysts produced by living organisms. The important stages of this biological transformation are summarized in Figures 2e, 2f, 2g, 2h, and 2i.

a. Action of enzymes⁶.—Enzymes in general are of a protidic nature. These catalysts influence the rates of reaction as a direct function of their concentration. To allow enzyme action, the substrate or substance to be transformed has to be present in a given concentration, an excess as well as a deficiency can paralyze the reaction. The accumulation of the reaction product also inhibits the transformation. Finally, the intensity of the enzymatic reaction depends also on temperature, pH etc.

Enzymatic reactions may be reversible, but they are characterized by their simplicity and by their specificity. In general, one enzyme is specialized in the catalysis of one reactant in a given reaction. The resulting transformation normally involves one specific group.



SCHEME 2e. RÉSUMÉ OF THE MAIN STEPS IN THE METABOLISM OF CARBON

Fig. 2e.—Summary of the main steps in the metabolism of carbon.

The activity of enzymes depends also upon the presence of natural adjuvants in the reaction medium: (1) the coenzymes, relatively small molecules which combine with the substrate to allow its transformation, (2) the oligo elements, (3) the inhibitors which can either block irreversibly the active centers of the enzyme or substitute themselves to the substrate (competitive inhibition).

b. Roles of the active particles of the cell.—Enzymes, or groups thereof, are located in the active particles of the cell. Therefore, the organites have well determined functions.

It should be born in mind, that the transformation of glucides into acetyl coenzyme A is not yet localized, but it is known that the mitochondrias produce

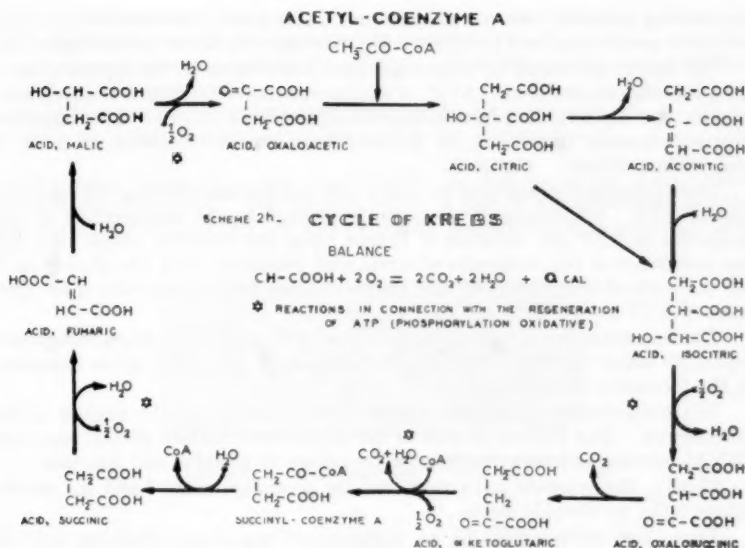


Fig. 2h.

the energy necessary for the cellular activity in form of organic substances able to accumulate such energy (adenosine triphosphate and similar substances).

The transformation of glucides, which nourish the cell, includes a number of reactions described in Figure 2g. These reactions result in the formation of acetyl coenzyme A, which is an active form of acetic acid of which one part is

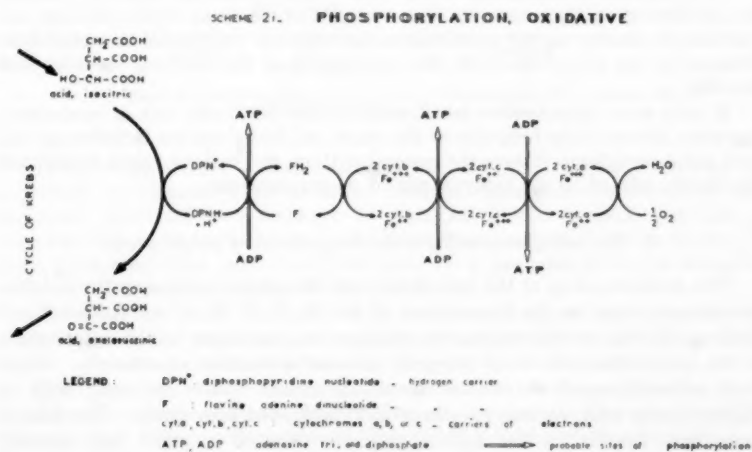


Fig. 2i.

the starting material for some biosyntheses (fatty acids, cholesterol etc.), while one other part is oxydized to CO_2 and H_2O through the Krebs cycle (Figure 2h).

The energy generated by these oxidations contributes to the regeneration of the adenosine triphosphate (ATP, or similar substances, cytidine triphosphate, uridine triphosphate, etc.) from adenosine diphosphate (ADP). This regeneration corresponds, depending on authors^{5,6}, to an accumulation of 8 to 13 kcal/mole available. Figure 2i.

The oxidation of acetic acid is not the only mechanism allowing the regeneration of ATP. Glycolysis for example is coupled to the regeneration of two molecules of ATP per molecule of hexose being converted to acetic acid, but the conversion of two molecules of acetic acid (resulting from the glycolysis of one molecule of hexose) to CO_2 and H_2O is coupled to the formation of 30 molecules of ATP from ADP.

The important role of the mitochondrias in the cell is therefore recognized, especially since the same particles also synthesize the amino acids necessary to the formation of proteins.

The biosynthesis of proteins appears to be localized in the nucleus of the microsomes. The nucleus as well as the microsomes contain ribonucleic acids (RNA), serving as a template for the formation of proteins and enzymes.

Finally, the plastids have each one its specialty, some build up starch, others build up steroids etc. . . .

Thus, the cell operates as an independent organism, receiving only its nourishment from the other cells. Inside the cell, specialized particles located in the cytoplasm convert raw materials into products necessary for themselves as well as into higher intermediates required by other organites.

The final or semifinal products have to diffuse through the membranes of the organites and here again, the cell shows a remarkable selectivity, as well in intracellular as in intercellular exchanges. A striking example is given by the cells of certain seaweeds which accumulate iodine in concentrations much above those of the medium they live in and under exclusion of other halogens.

This selective permeability makes experimentation more difficult, because the biochemist making some starting material available to whole cells can not conclude in absence of any metabolism, that the cell was unable to metabolize, because he has no evidence for the penetration of the starting material into the cell.

It may seem fastidious to recall, even briefly (and with risk of confusion), the main points of the behavior of the plant cell, but since the laticiferous cell, with some exceptions, follows the general pattern, the various points mentioned are closely related to the biosynthesis of *cis*-polyisoprene.

3. The laticiferous cell and the biosynthesis of polyisoprene

The understanding of the laticiferous cell has greatly advanced through the recent work done in the laboratories of the N. R. P. R. A. by Andrews and Dickenson⁷, who have developed an experimental technique for the examination of the laticiferous cell in its integrity under the electron microscope. Their work primarily confirms the fact that laticiferous vessels are truly built of anastomosing cells, as many authors had mentioned previously. The laticiferous cells exhibit all the known characteristics of a plant cell, namely (Figure 2j):

- a cellulosic envelope,
- against this envelope, a cytoplasmic membrane,
- a nucleus squeezed against the cell walls and separated from the cytoplasm by a thin membrane,
- mitochondrias recognizable by their particular morphology,
- an endoplasmic reticulum associated to the microsomes.

The latex filling the major part of the cell has no visible delimitation towards the cytoplasm. The latex therefore is part of the cytoplasm but the organites mentioned earlier are less numerous than the typical latex particles.

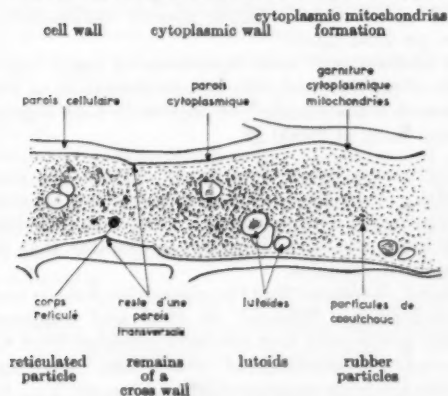
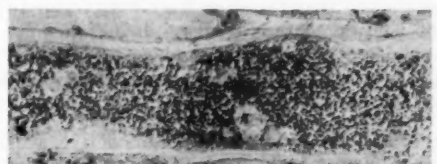


FIG. 2j.—Electron microscope photograph of part of a laticiferous cell⁷. Approx. 3000 X. Identification of latex particles is possible.

The latex particles are of three kinds: (1) the rubber globules isolated by a protidic membrane, (2) B spherical particles (nomenclature chosen by the authors), which are very sensitive to variations in the medium and have a diameter of 1 to 3 μ and contain fibrous protidic substances, forming the major part of the nonrubber particles of the latex, (3) C particles of similar diameter as B and containing smaller spherical inclusions.

These authors⁸ also state, that the latex obtained by tapping contains in its fresh state all the particles and organites described before as well as some nuclei. But the mitochondrias are less frequent than in the cell.

The C particles contained in the latex would resemble the particles described by Frey-Wyssling⁹, while the B particles can be identified as the "lutoids" discovered in 1948 by Homans and Van Gils¹⁰. Verhaar¹¹ in turn identified them in 1952 under the name of "viscoids".

Few hypotheses have been ventured concerning the function of the particles of Frey-Wyssling. On the contrary, many indications have been found as to the importance of the lutoids.

Prior to the late discovery of the lutoids, which is due to their short life-time after tapping, Schmidt¹² (1882) has assimilated the latex to the content of the vacuoles of the laticiferous cell and later, Popovici¹³ followed by Bobiliov¹⁴ maintained that the rubber particles were generated in the cytoplasm and were then ejected into the vacuole. The discovery in 1948 of the lutoids modified the earlier theories and Schweitzer¹⁵ then suggested that the particles originate in the sieve tubes of the bast, but Ruinen and de Haan-Homans¹⁶ concluded that they could not possibly migrate from the sieve tubes towards the laticiferous vessels and that therefore they were formed "in situ"; Schoon and Phoa¹⁷ in 1956 considered the lutoids as being vacuoles where the polymerization of *cis*-polyisoprene would take place. Wiersum¹⁸ in 1957 demonstrated the vacuolar nature of the lutoids by colorimetric methods.

Two facts should be mentioned:

a. Teas¹⁹ observed, that by incubating radioactive acetate in latex previously centrifuged at 9000 g and therefore separated from lutoids, the polyisoprene recovered would have a higher specific radioactivity than normal preparations based on fresh latex.

b. Archer and McSweeney²⁰ have demonstrated lately that the final phase in the biosynthesis of polyisoprene, the polycondensation of isopentenyl pyrophosphate, occurs even if the lutoids had previously been eliminated by centrifugation of the fresh latex at 29000 g.

These two experiments prove that the lutoids do not participate in the formation of rubber, since they are unnecessary to the conversion of the acetate and the isopentenyl pyrophosphate. They can therefore be considered as being relatively inert, which confirms the assumption that they can be considered as polydispersed vacuoles.

On the other hand, it follows that the *cis*-polyisoprene is synthesized in the cytoplasm as indicated by Milanez²¹ in 1946 and confirmed recently by Southorn²². Added to the fact, that the latex collected from the tapping contains all the elements characteristic of intact cells, including vacuoles, this brings us to consider the latex as being a laticiferous cell from the physiological point of view. Of course, the intensity of the exchanges might not be the same in both cases. This concept is very important, because it validates the results of earlier research done with fresh latex as an enzymatic medium and indicates that this exudation is a choice material for the study of the biosynthesis of polyisoprene.

Already certain results confirm this identity between the behavior of latex and that of a cell:

a) Gascoigne and coworkers²³ succeeded in characterizing in fresh latex a specific enzyme for the glycolysis: the aldolase (cf. Figure 2g: transformation of fructose-1, 6-diphosphate).

b) Van Der Tempel²⁴ and Hsia²⁵ have demonstrated that fresh latex eliminates carbon dioxide and absorbs small amounts of oxygen.

c) Fournier and coworkers²⁶ have indicated, that the fresh latex transforms sodium acetate 2¹⁴C in vitro, not only to polyisoprene which had already been proven, but also to acids of the Krebs cycle.

d) M. McMullen²⁷ has detected ribonucleic acids in latex.

These activities of the latex are also characteristic of living cells and indicate the presence in this medium of fundamental organites such as the mitochondrias, the microsomes etc.

Fresh latex as enzymatic medium is comparable to the medium currently used in animal biology for the enzymatic study of tissues such as the liver, the heart, etc. . . . This method consists in finely crushing the material with a special apparatus, so as to burst the cells. By centrifuging the resulting liquid, the remains of the cellular wall are separated from the medium which contains all the particles of the cell. The use of this medium for carrying out enzymic reactions has proven to be very fruitful, even if not all of the chondriome was recovered. In fact, the specific permeability of the cell is no longer a problem and by using this procedure, marked substances identical to those produced *in situ* can be introduced in a liquid equivalent to the cytoplasm, and this without any doubt as to their penetration into the cell.

All the work done in the field of biosynthesis of *cis*-polyisoprene is more or less based upon the study of the metabolism of one or several properly chosen substances. It is understood that the way of introduction of the substance can have a preponderant influence upon the results obtained. We will therefore evaluate the results described in the literature according to the dependability of the manner of introduction of the substance.

It is impossible to say at this time whether the rubber globule can be considered as a plastid. This problem will only be solved, when the last step of the formation of *cis*-polyisoprene will be located accurately in one specific type of intracellular particle.

This background throws into relief the complexity of a plant cell; the laticiferous cell does not escape this rule. Ultimately, thousands of reactions contribute to the formation of rubber, since we have to include the synthesis of enzymes, proteins etc., which occur at some point within the mechanism. All this takes place in a cell the dimensions of which are of the order of one hundredth of a millimeter.

III. THE FIRST APPROACHES TO THE PROBLEM OF THE BIOSYNTHESIS OF RUBBER

Interest in the problem of rubber synthesis in plants was aroused many years ago, but the important milestones in the discovery of the synthesis mechanism date from the time between 1950 and 1960:

- In 1950, Bonner and Arreguin^{28,29,30} demonstrated the role played by acetic acid in the formation of rubber.
- In 1956, Teas¹⁹ indicated that the latex was able to transform acetic acid into polyisoprene *in vitro*.
- In 1958, two years after the discovery of mevalonic acid, Park and Bonner²¹ proved that this acid is an interesting precursor for rubber.
- In 1960, Lynen³² used latex as an enzymatic medium to verify that isopentenyl pyrophosphate is transformed into high molecular weight polyisoprene.

However, the biogenesis of rubber always impassioned the mind and numerous theories were proposed long before experimental techniques were available for their verification. We shall refrain to judge such speculations in the

light of today's knowledge, since our own theories may some day encounter the same fate.

A. THE THEORIES PREVIOUS TO 1950

The oldest theory is due to Harries³³ in 1919 and is based on the fact that the ozonolysis of rubber yields levulinic acid. Harries assumes therefore that the pentadienyl radical is the unit which condenses to form rubber (Figure 3a).

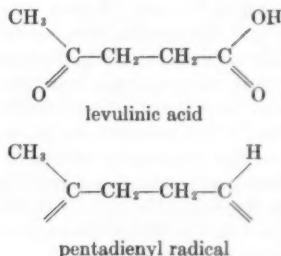


FIG. 3a.—Precursors of rubber, according to Harries.

The theories may be classified according to the compounds postulated as precursors of rubber.

A first school of thought considered the versatile glucides (carbohydrates) to be the source of rubber:

Steward³⁴ in 1931 suggested a mechanism based upon the formation of the isoprenic skeleton through condensation of glucides such as aldopentose, apiose, . . .

Hall³⁵ took up this idea in 1935 and proposed a reaction scheme starting from C⁶ glucides and involving complex glucidic acids.

Nerdel³⁶ expounded a similar theory, where the condensation of ketoses

would occur through the group $\text{C}=\text{O}$.

Another school believes isoprene to be a direct precursor of rubber:

Aschan³⁷ in 1929, Ambros³⁸ in 1937 and Prokofiev³⁹ in 1939 tried to demonstrate that isoprene is an active promoter of rubber and were encouraged by the opinion voiced by Robinson⁴⁰ at the Chemistry Congress of Madrid in 1934. Ambros³⁸ for example demonstrated the ability of latex serum to polymerize isoprene in the presence of hydrogen peroxide, but today this fact is attributed to redox activation and not to enzymatic action, which is known to vanish after treatment of the latex.

Frey-Wyssling⁴¹ in 1945 voiced the opinion, that isoprene originated from apiose, a glucide often found in nature.

Zelinsky⁴² in 1940 assumed that ethylene and butadiene play a certain role.

One finds then in the literature isolated theories, such as that of Hesse⁴³ (1941), who proposed the following scheme (Figure 3b):

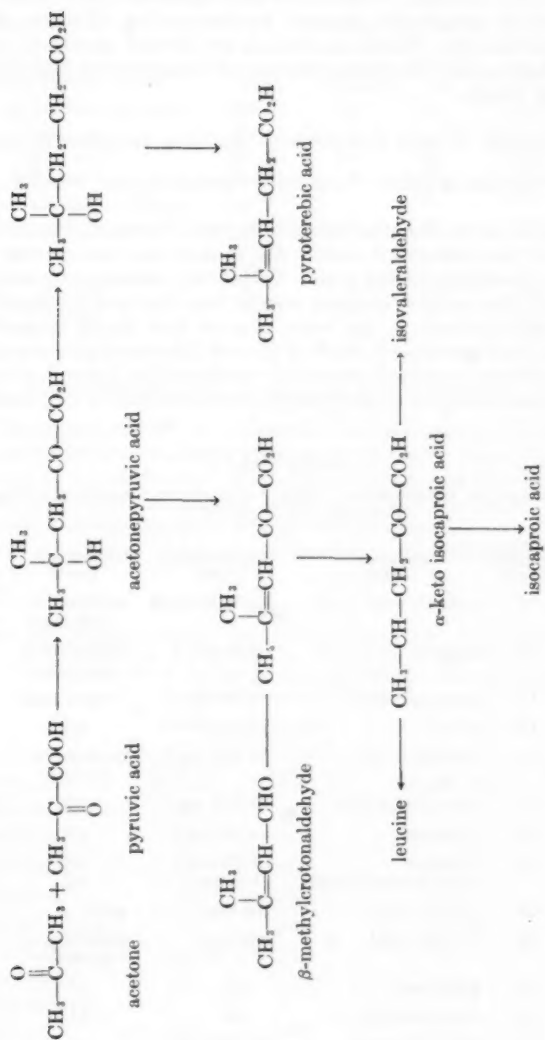


FIG. 3b.—Scheme of Hesse, the precursors of rubber.

Leucine, isocaproic acid and isovaleraldehyde would be the precursors of rubber, of which they have the basic structure.

For de Wildemann⁴⁴ (1944), there is no doubt that: "the crude rubber, complex plant hydrocarbon, is formed by polymerization and condensation of terpenes, proteinic compounds, starches, tannins, rosins, alkaloids, glucosides, mucilages, enzymes etc. These compounds are formed mostly by photosynthesis in the buds and in the young leaves. Polymerization may continue in the laticiferous vessels. . . ."

Drobkov⁴⁵, 1946, thought that polyisoprene forms according to the process:

Inulin \rightarrow monosaccharide \rightarrow acetone \rightarrow acetaldehyde \rightarrow rubber.

In an excellent word of caution published in 1945, Polonovski⁴⁶ underlined that the weakness of such theories is mainly due to their discrepancy with the facts or to a lack of knowledge at the time. Polonovski, reasoning by analogy, was first to suggest that *cis*-polyisoprene results from the polycondensation of a phosphorous intermediate, in the same manner that starch is produced by polycondensation of phosphoric esters of glucose (glucose-1-phosphate). Only in 1960 this brilliant hypothesis was solidly confirmed by Lynen³², after demonstrating the transformation of isopentenyl pyrophosphate to polyisoprene.

TABLE IIIA
SUMMARY OF EXPERIMENTS WITH INEFFECTIVE COMPOUNDS BY
BONNER AND ARREGUIN

Temperature of the greenhouse	Duration of experiment in days	Substance added	Concentrations used	Effect upon growth	Rubber formed
80° F	14	pyruvic acid	10-1000 mg/l	inhibitor at 100 mg/l	nil
80° F	14	sucrose	5-20 g/l	reduction in growth	nil
80° F	14	crotonaldehyde	1-100 mg/l	1 mg/l toxic	nil
80° F	14	citral	10 mg/l	nil	nil
80° F	14	acetaldehyde	10-100 mg/l	increase in growth	nil
80° F	14	isovaleraldehyde	10-100 mg/l	nil	nil
80° F	14	α pinene	10-90 mg/l	nil	nil
80° F	14	limonene	10-90 mg/l	nil	nil
80° F	14	oil of guayule leaves	1-9 mg/l	nil	nil
80° F	28	succinic acid	100 mg/l	toxic	nil
80° F	28	fumaric acid	100 mg/l	reduction of growth	nil
80° F	28	citric acid	id.	id.	nil
80° F	28	isovaleric acid	id.	id.	nil
days 65° F night 55° F	28	tiglic aldehyde	10-100 mg/l	nil	nil
—	—	tiglic acid	10-100 mg/l	nil	reduced
—	—	valine	10-100 mg/l	nil	nil
—	—	leucine	10-100 mg/l	nil	nil

TABLE IIIB

EFFECT OF ACETATE UPON THE RUBBER FORMATION IN THE GUAYULE PLANT
Duration of the experiment: 28 days
Initial rubber content: 0.00

Addition to the base solution	Temperature	Weight of dry material per plant		% rubber	Rubber, mg/10 plants
		Roots and stems, mg	Leaves, mg		
Nil, plants for final reference	80° F	42	69	0.14	0.59
Acetate: 10 mg/l	80° F	41	62	0.25	1.02
100 mg/l	80° F	33	50	0.27	0.89
1000 mg/l	80° F	9	13	0.00	0.00
Nil, plants for final reference	80° F (day) 56° F (night)	16	19	0.31	0.50
Acetate: 10 mg/l	10° F	16	19	0.44	0.70
100 mg/l	10° F	13	13	0.57	0.74
1000 mg/l	10° F	7.6	9.6	0.28	0.21

B. THE CONTRIBUTIONS OF BONNER AND COWORKERS (1950)

After the second world war, radioactive isotopes became available and biochemical methods⁴⁷ were radically changed by the use of the carbon 14, tritium, phosphorous 32 and sulfur 35. Thus, the evolution of a given compound can be followed stepwise in a complex medium, even hardly perceptible amounts can be traced through elaborate weight determinations.

Through a judicious choice of the position of the radioactive atom within

TABLE IIIC

EFFECT OF ACETONE AND OF THE MIXTURE ACETONE AND ACETATE UPON THE RUBBER FORMATION IN YOUNG GUAYULE PLANTS
Culture at 65° F during the day and 55° F during the night
for a period of 14 days

Substances added	Weight of dry material per plant		% total rubber	Rubber, mg/10 plants
	Roots and stems, mg	Leaves, mg		
Initial value of reference	27	115	0.20	0.54
Nil final reference	71	146	0.30	2.13
Acetone 100 mg/l	70	145	0.44	3.08
Acetone 1000 mg/l	65	176	0.52	3.38
Sodium acetate 10 mg/l	65	129	0.52	3.38
Sodium acetate 100 mg/l	60	111	0.40	2.40
Acetone 100 mg/l + acetate 10 mg/l	43	141	0.36	1.55
Acetone 100 mg/l + acetate 100 mg/l	50	142	0.36	1.80
Acetone 1000 mg/l + acetate 10 mg/l	64	126	0.40	2.56
Acetone 1000 mg/l + acetate 100 mg/l	48	127	0.39	1.87

TABLE IIIId

Substances added	Weight of dry material per plant		% of total rubber	Rubber, mg/10 plants
	Roots and stems, mg	Leaves, mg		
Initial reference	65	24	—	—
Final reference	39	56	0.12	0.47
Sodium acetoacetate 10 mg/l	43	65	0.33	1.42
β -Methylcrotonic acid 10 mg/l	38	66	0.23	0.87

the molecule of the compound, the most complex structural problems can be solved.

The analytical sensitivity has been considerably improved by the use of new techniques, now in full development, such as paper and column chromatography, electrophoresis, and spectrography, thus making possible the discovery of phenomena well beyond the sensitivity of any analytical balance.

Only compounds in very low molar concentrations of about 10^{-3} may be added to biological media and since only a few milliliters of such media are usually involved, it becomes necessary to follow the course taken by a few micromoles (10^{-6} moles), after numerous and often divergent transformations.

At the time these new techniques became available, Bonner and Arreguin undertook one of the most satisfactory projects, by using labelled molecules during the third part of their study³⁰. In the first part of their work, they attempted to demonstrate the influence of certain nontagged substances upon the quantity of rubber formed in the young guayule plant (*Parthenium argentatum*).

During this study, young plants (2 to 4 months) were placed in flasks, closed with cork stoppers with a hole for the stem of the plant. The flask contained 15 ml of a nutrient medium to which an acetone extract of guayule leaves was added. To this medium were added a number of test compounds. Each week, the nutrient medium was renewed.

Bonner and Arreguin first showed that a number of compounds were ineffective (Table IIIa).

On the contrary, in the same conditions, the addition of sodium acetate (Table IIIb), or acetone (Table IIIc), or a mixture of both (Table IIId), had a marked effect on the rubber amount formed in the experimental plants.

These two groups of results led them to think that sodium acetoacetate and β -methylcrotonic acid could well be the products resulting from the metabolism of sodium acetate or of acetone.

The experimental findings confirmed their views (Table IIId) and they concluded, that the biosynthesis of rubber probably follows this sequence (Figure 3c):



FIG. 3c.—Sequence of Bonner and Arreguin.

The second part of their paper²⁹, duplicating their first experiments with cultures of tissues and no longer with plants, confirms the first part.

By using sodium acetate labelled with carbon 14 in the third part of their study³⁰ they can draw a balance of the acetate used by the plant and demonstrate beyond doubt, that the rubber formed during the experiment comes exclusively from the marked acetate.

Bonner and Arreguin (see page 1247, first experiment) have nourished a plant with sodium acetate uniformly marked to give 10^3 counts per minute and per mg (cpm/mg). It is known, that during the experiment about 0.3 mg of rubber is formed, diluted in the total of 13 mg contained in the plant. These 13 mg have a specific activity of 35 cpm/mg, or a total activity of $35 \cdot 13 = 555$ cpm. The amount of rubber synthesized and exclusively responsible for the radioactivity is 0.3 mg and corresponds to a specific activity of

$$\frac{555}{.3} = 1.5 \cdot 10^3 \text{ cpm/mg}$$

This specific activity is of the same order as that of the initial acetate. There is no doubt, that the rubber formed during the experiment originates only from the labelled sodium acetate placed in the nutrient medium. Consequently, it appears that the very simple structure of the promoter was integrated without change into polyisoprene.

This last experiment of Bonner and Arreguin concerning the reaction sequence shows that:

1. The acetate is an intermediate in the biosynthesis of rubber.
2. The method used is promising.

However evident these two points, the lessons drawn from the study of Bonner and Arreguin were not immediately accepted and a number of contributions were then published, some of which leading their authors to controversial conclusions.

C. STUDIES LEADING TO DOUBTFUL CONCLUSIONS

In 1950, Johnson⁴⁸ fed young *cryptostegia grandiflora* plants with a number of compounds of structures resembling isoprene, namely alcohols and acids with isoprenic structure. Certain substances were poisons for the plant, others had no effect upon rubber production, and only isoprene glycol gave an appreciable result. Johnson also indicated that β -methylcrotonic acid had no influence, contrary to a statement by Bonner and Arreguin.

Johnson's work suggests two remarks:

1. The method for evaluating the amount of rubber formed (intensity of coloration with sudan III or oil red) is not very accurate.
2. For reasons already discussed (see page 1249), there is no certainty as to the transformation without previous modification of isoprene glycol to rubber. This invalidates all structural considerations.

Two theses from Cornell University presented in 1955 by Springborn⁴⁹ on the metabolism of Hesse's precursors (cf. page 1244) and by Chadha⁵⁰ on the

metabolism of isoprenic alcohols are a continuation of the first studies by Johnson. In 1954, Chrastil¹² published a paper on the influence of certain substances upon the rubber content of *Kok-saghyz* by either application on the leaves or injection at the base of the leaves. The results given in Table IIIe suggest to Chrastil, that the rubber in the plant is destroyed by acetone, dihydroxyacetone and pyruvic acid. On the contrary, the rubber content is increased by addition of inositol, acetic acid, ethyl acetylacetate or adenosine triphosphate.

TABLE IIIe
RESULTS OF CHRASTIL'S EXPERIMENTS WITH *KOK-SAGHYZ*

Substances injected	Dry material %	Rubber % of dry material
Control	33.3	4.83
ATP (0.5%)	39.3	6.98
NaF (0.01 M)	36.7	5.98
Fructoidase	34.6	4.91
Dihydroxyacetone (3%)	30.3	3.60
Pyruvic acid (3%)	31.0	0.50
Inulin (10%)	35.2	4.66
Control	23.9	2.50
Glucose (5%)	24.2	4.90
Acetic acid	25.6	12.90
NaF	25.2	6.40
Inositol (5%)	24.9	8.28
Acetone (1%)	24.5	1.30
Pyruvic acid (3%)	23.9	1.63
Acetoacetate ethyl	25.75	32.30
Fructose 10%	24.9	26.80
Malonic acid (0.5%)	24.0	26.60
Succinic acid (2%)	24.7	3.18
As ₂ O ₃ + (0.002 M)	24.8	13.90
Gluconic acid	24.95	4.28

Chrastil then observed, that the inhibitors of the Krebs cycle—such as malonic acid or arsenous oxide—or of glycolysis—such as sodium fluoride or sodium nitrite—caused a considerable increase in amounts of rubber formed by the plant. From this, he concluded that the formation of rubber included neither glycolysis nor the Krebs cycle.

The study by Chrastil with the plant as a whole shows, that applying a product on the leaves does not allow one to distinguish between a stimulating effect, as by adenosine triphosphate, and a metabolism of a carbon source such as inositol or apiose.

His conclusions relative to the influence of the inhibitors require knowledge of their exact effect upon the photosynthesis as well as upon the plant life. Only then could one be certain that the increase in rubber content in the dried extract of the plant is not due to heavy utilization of the reserves, following an interruption of the photosynthesis. This would falsify the relation:

$$\frac{\text{weight of rubber}}{\text{weight of dry substance}}$$

Vyvalko and collaborators^{52, 53, 54} and Chilov⁵⁵ were having the same sort of experience in 1956 by applying to the leaves of Kok-saghyz a number of marked glucides as well as various other substances, but conferring only little radioactivity to the rubber. They found that labelled α -alanine (α -alanine 2^{14}C) was transformed into rubber more readily than acetic acid 2^{14}C (Table IIIf), the contrary being the case for carotene.

From this, they concluded that acetic acid was not a direct promoter for rubber and that carotene and polyisoprene were formed by different mechanisms. They also indicated, that α -alanine 1^{14}C did not yield radioactive rubber. Therefore, only the carbons in 2 and 3 positions participated in this biosynthesis. Based upon their first observation, they imagined a reaction sequence including the decarboxylation of α -alanine to a two carbon imine and then to acetaldehyde which would react with triose to yield a direct precursor of rubber.

These conclusions are no longer valid if acetic acid and α -alanine are injected into the roots (Table IIIf). These two promoters, as pyruvic acid, give the

TABLE IIIf

RESULTS OF THE EXPERIMENTS OF VYVALKO AND COLLABORATORS ON KOK-SAGHYZ

Substances introduced	Way of introduction	
	Leaves, radioactivity relative to rubber	Roots, radioactivity relative to rubber
Experiments of 1955		
Acetic acid 1^{14}C (control 100)	100	100
Saccharose 1^{14}C	100	100
Glycocoll 1^{14}C	67	70
Alanine 1^{14}C	14	—
Alanine 2^{14}C	300	—
Pyruvic acid 2^{14}C	30	100
Benzoic acid 2^{14}C	28	—
Experiments of 1956		
Acetic acid 1^{14}C (control 100)	100	100
Alanine 2^{14}C	400	100
Acetoacetic acid 3^{14}C	100	20
Methylcrotonic acid 3^{14}C	30	25
Glyceric acid	75	—

same radioactivity to rubber. Radioactive pyruvic acid is a promoter equivalent to acetic acid and to α -alanine, if injected at the roots; this contradicts the opinion of Chrastil⁵¹ (see page 1250) concerning the destruction of rubber already formed in the plant. It would show that the leaf of Kok-saghyz preferentially lets α -alanine penetrate to the laticiferous cells and acetic acid preferentially to the plastids forming the carotenes, while the root equally absorbs both.

Even if the two modes of introduction would prove that α -alanine is more efficiently incorporated than acetic acid, it would be questionable to conclude that this amino-acid is included in the synthesis mechanism of rubber because of its particular structure. Teas and Bonner⁵⁶ stated that, in general, α -alanine

was readily transformed into pyruvic acid which in turn formed acetyl coenzyme A, the acetyl group corresponding in fact to the carbons in position 2 and 3 of the α -alanine in question. This mode of formation of acetyl coenzyme A occurs naturally if coupled with the decarboxylation of pyruvic acid. But the transformation, after direct injection into the cell, of acetic acid into acetyl coenzyme A requires a secondary enzymatic reaction relative to the normal cell activity and this would explain the better yield obtained with α -alanine without eliminating acetic acid as a precursor of rubber.

Barlow and Patrick⁶⁷ have reported an example which clearly demonstrates the implications of this kind of experiment upon the entire plant. These authors have treated the leaves of a 2 year old hevea plant with a solution of marked mevalonic acid. Its penetration is fast. The analysis of the leaves shows that 52% of the initial amount of precursor was recovered unconverted, 48% was transformed into carotene and the rubber was unmarked.

Barlow and Patrick did not deny the role of mevalonic acid and gave no conclusion to their study. But it is entirely possible that mevalonic acid easily reaches the carotene forming cells and hardly any laticiferous cells, since it is known that mevalonic acid is transformed by the latex into *cis*-polyisoprene with excellent yields. This experiment perfectly illustrates the difficulties encountered while studying the role of a precursor in an entire plant.

D. CONCLUSIONS

The preceding discussion shows what a delicate science plant biology still is today, stepwise feeling its way along, despite the use of the most modern techniques. During this transition period, various studies were made and published. They were based on unbiased experimental results, but suggested conclusions, which can no longer be upheld. In particular, to study a mechanism taking place in specialized cells on an entire plant leads to confusing results because it is uncertain what part other cells play in the transformation of the precursor to be tested.

Animal physiology does not encounter these difficulties, because the organ to be studied can be readily isolated, and the content of specific cells can be collected. In these conditions the specificity of transformations taking place in a given type of cell is respected. Therefore the studies made with animal tissues have allowed them to reveal step by step the mechanism of the biosynthesis of terpenes.

It is therefore impossible to ignore the studies made on the formation of terpenes, especially since in contrast to the earlier work mentioned, they were analyzed with a scientific precision which warrants the conclusions reached.

As the result of these studies, the biosynthesis of *cis*-polyisoprene appears as a particular case of the genesis of the terpenes, the facts supporting this view will be presented in section IV.

IV. THE BIOSYNTHESIS OF TERPENES

Despite an apparently endless diversity, life is ruled by a small number of common laws. Basic metabolisms in particular are essentially the same in plant life as in animal life, from one species to another. In general, glycolysis and the Krebs cycle are universal reactions. Among these common reactions can now be counted the fatty acid cycles and the biosynthesis of terpenes.

Since Ruzicka⁵⁸ in 1922 announced the famous isoprene rule, the unity in the formation of terpenes has been anticipated, but only in 1958 was it verified. This verification is one of the most fascinating examples of scientific competition, because it was the result of studies made by numerous independent groups, each one contributing to the final success. In addition, this distribution of work has allowed each one to specialize in his own area and the result is of impressive quality.

This part of the discussion is made difficult because of the accuracy of the demonstrations and the particular methods of deduction relied on. For the benefit of those readers who are not familiar with enzymology, *we shall precede each principal section with a short summary of the discussion to follow.*

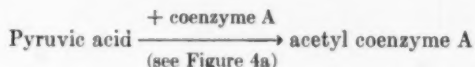
A. FORMATION OF THE BRANCHED STRUCTURE

1. Formation of acetyl coenzyme A

Summary: Acetic acid can only be metabolized in form of a thioester of the coenzyme A (Co A). The acetyl coenzyme A is produced by decarboxylation of pyruvic acid concomitant to the condensation with coenzyme A. Acetyl coenzyme A can also result from degradation of fatty acids.

Acetic acid is produced by degradation either of glucides or of fatty acids. Both mechanisms are now well known and both yield not free acetic acid, but a derivative which is biologically active: acetyl coenzyme A.

a. Formation of acetyl coenzyme A by glycolysis.—The principal steps of the glycolysis (Figure 2g) do not require further discussion, but it is necessary to comment on the last step of the reaction sequence:



and particularly the mechanism of coenzyme A intervention.

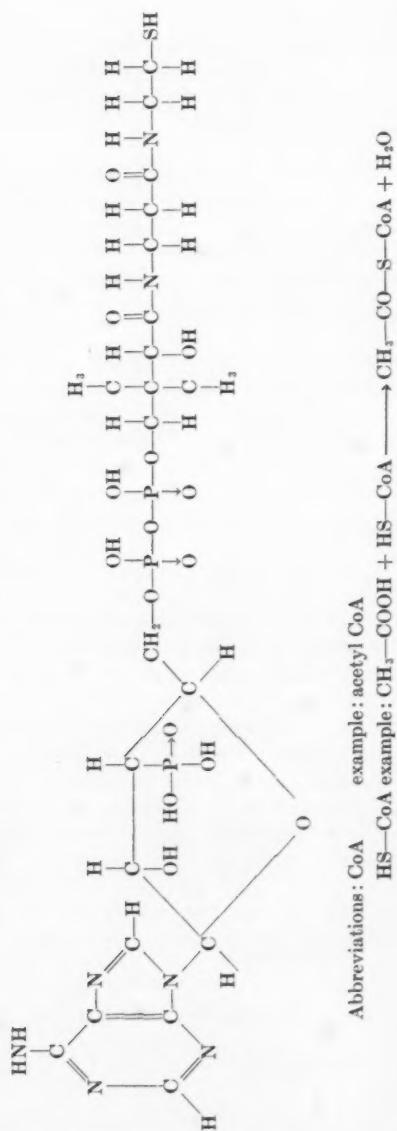


FIG. 4a.—Structure of coenzyme A.

The formation of acetyl coenzyme A requires the presence of diphospho thiamine (DPT), lipoic acid, CoA, DPN and an enzyme named pyruvic oxidase. Whether the latter is an enzyme by itself⁵⁹ or a complex formed by several enzymes is still subject to discussion⁶⁰. The reactions of Figure 4b presumably take place.

- (1) Pyruvate + DPT \longrightarrow addition compound + CO₂
 - (2) Addition compound + oxidized lipoic acid \longrightarrow DPT + acetyl lipoic acid
 - (3) Acetyl lipoic acid + CoA \longrightarrow lipoic acid + acetyl CoA
 - (4) Lipoic acid + FAD* \longrightarrow oxidized lipoic acid + FADH₂
 - (5) FADH₂ + DPN* \longrightarrow FAD + DPNH₂
- Total: Pyruvate + CoA + DPN \longrightarrow acetyl CoA + DPNH₂ + CO₂

FIG. 4b.—Transformation of pyruvic acid to acetyl coenzyme A.

This reaction sequence can be represented schematically as in Figure 4c.

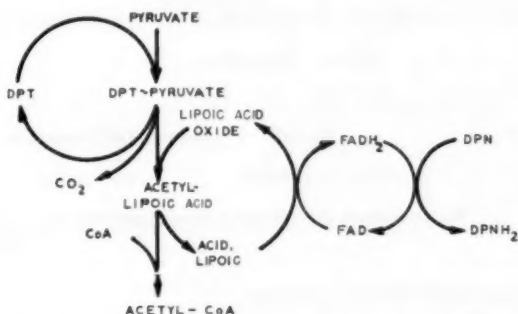


FIG. 4c.—Formation of acetyl coenzyme A from pyruvic acid.

For some time it had been postulated, that the addition compound, DPT pyruvate, could result from a scission of the thiazole nucleus of the cocarboxylase (DPT) with formation of a sulfhydryl group which would react with the carbonyl group of the pyruvate (Figure 4d).

* FAD, FADH₂: flavine adenine dinucleotide oxidized, reduced. DPN, DPNH₂: diphosphopyridine nucleotide oxidized, reduced. These substances act as oxygen or hydrogen transfer agents.

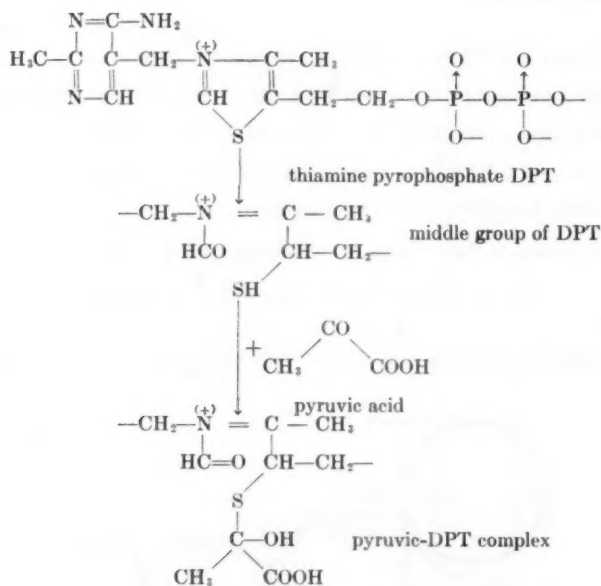
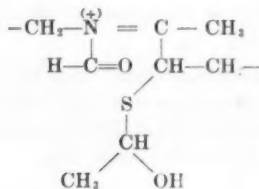


FIG. 4d.—Details of the formation of acetyl coenzyme A.

The complex would decarboxylate to:



The following reaction would be written according to Figure 4e.

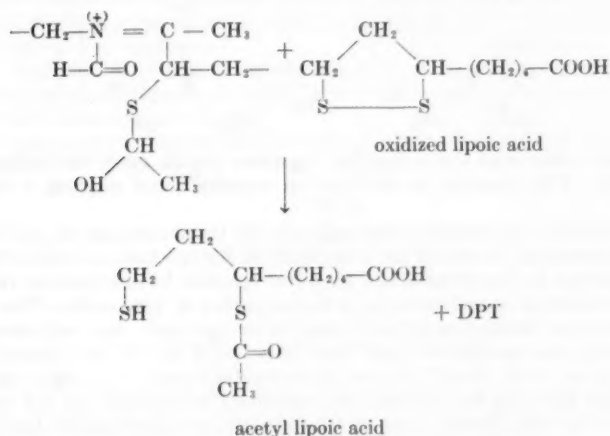
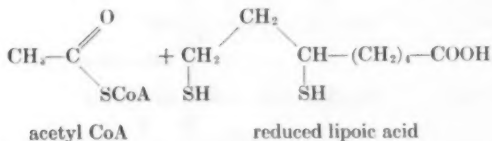
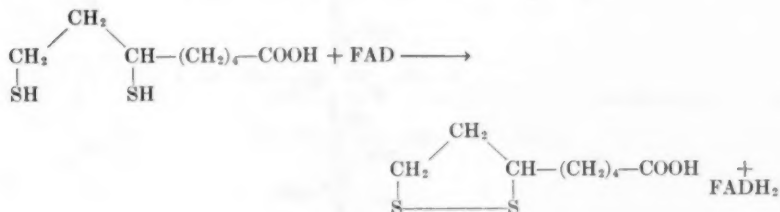


FIG. 4e.—Intermediate reactions of lipoic acid.

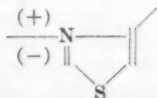
The acetyl group is transferred over to free coenzyme A, which produces:



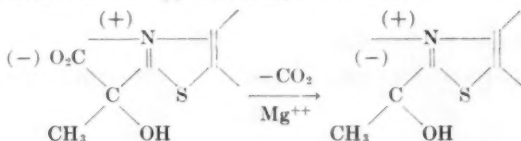
The reoxidation of lipoic acid is assured by flavine adenine dinucleotide (FAD)^{61, 62, 63}:



But Breslow⁶⁶ proposed to write the active form of DPT in a different way, in considering the condensations of the benzoin and furoin type⁶⁴, the conversion of pyruvic acid to acetaldehyde or acetoin⁶⁵ catalyzed by thiazolium salts, where an "active aldehyde" occurs as intermediate, or finally the rapid exchange with D₂O on the carbon atom situated between the nitrogen and the sulfur atom.



Through condensation with pyruvic acid, the reaction:



would take place and the remaining reactions would occur as indicated in Figure 4e. This reaction is sensitive to arsenite⁶⁷ and requires a bivalent cation⁶⁸.

This review of mechanism intervening in the transformation of pyruvic acid to acetyl coenzyme A sets off the complexity of the reactions as well as the fact that coenzyme A is acetylated not by direct reaction but by transfer reaction.

b. Formation of acetyl coenzyme A by β -oxidation of fatty acids.—The details of the principal metabolism of fatty acids have been uncovered only recently⁶⁹, even though the mechanism itself had been found in 1904 by Knoop⁷⁰, who marked atoms with phenyl groups (phenyl-substituted fatty acids) and concluded that the oxidation started and continued in β -position to the carboxyl group. Other oxidation processes for fatty acids are known today, but the one involving the β -position remains physiologically the most important and is the only one of interest in the biosynthesis of terpenes. The reaction takes place in 5 steps (Figure 4f).

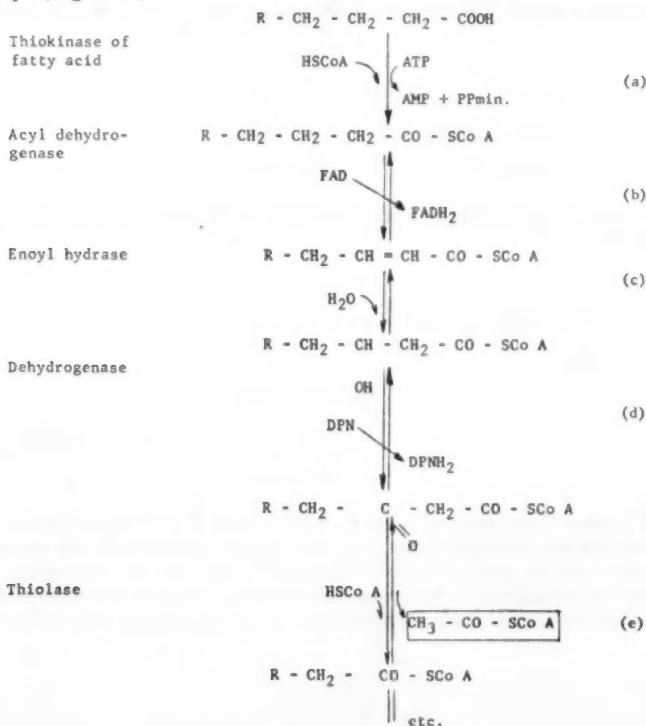


Fig. 4f.—Oxidation process of fatty acids.

It is remarkable, that the initial activation of fatty acid with reaction of one molecule of adenosine triphosphate (ATP) is sufficient to operate this sequence of reactions which produces one molecule of acetyl Co A as a result of scission-transfer due to the thiolase.

The reaction (a) of Figure 4f was studied by measuring either the disappearance of the thiol group of Co A⁷¹, or the appearance of the pyrophosphoric ion⁷², or the disappearance of ATP.

The magnesium ion is essential, because it forms a chelate with the enzyme, Co A and ATP⁷³ (Figure 4g).

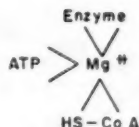


FIG. 4g.—Complex: enzyme—ATP—Mg—Co A.

During the formation of the complex, the entropy of the system decreases and with it decreases the activation energy. This chelate would react with a fatty acid $R-CH_2-CH_2-CH_2COOH$ according to Figure 4h.



FIG. 4h.—Action of magnesium chelate ion during the reaction of coenzyme A.

The reaction (b) (Figure 4f) is catalyzed by acyldehydrogenase having riboflavines as prosthetic groups. Several acyl dehydrogenases exist, each one operating for only a certain number of fatty acids of given chain length. The oxidation yields *trans* unsaturated esters⁷⁴.

In general, the enzyme-substratum complex is difficult to isolate because of its instability, but the chelate formed with magnesium ion is stable enough to resist dialysis and precipitation. Riboflavines associated with acyl dehydro-

genases are quite stable to air, which is rather uncommon. Beinert and Page⁷⁵ assume two prosthetic groups FAD per molecule of acetyl dehydrogenase (Y) and, on the basis of spectroscopic measurements, propose the sequence in Figure 4i to illustrate this reaction:

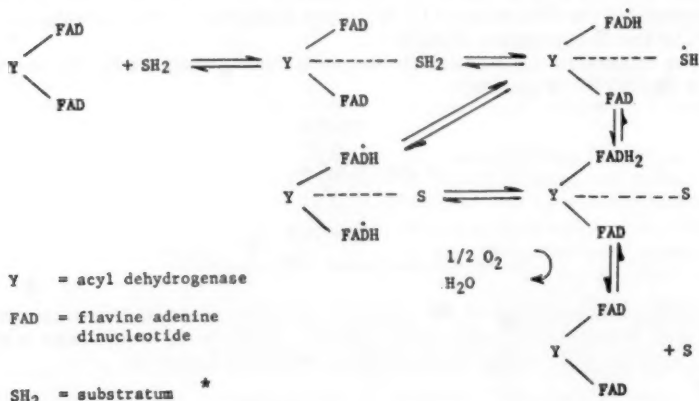
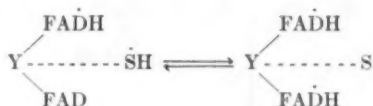


FIG. 4i.—Reaction mechanism of acyl hydrogenase according to Beinert and Page.

These facts are important, because they support the theory of an intermolecular complex enzyme-substratum. They also lead to the conclusion that the free radicals are unstable at normal temperatures, owing to their increase in reactivity and not to their particular structure, because in the absence of further reaction, the equilibrium:



is relatively stable.

The hydration reaction (c), Figure 4f, is regulated by the enoylhydrase which apparently is only slightly influenced by the carbon chain length of the acid, or the *cis-trans* configuration. The α - β -*trans* unsaturated ester is hydrated to L- β -hydroxyacetyl ester:



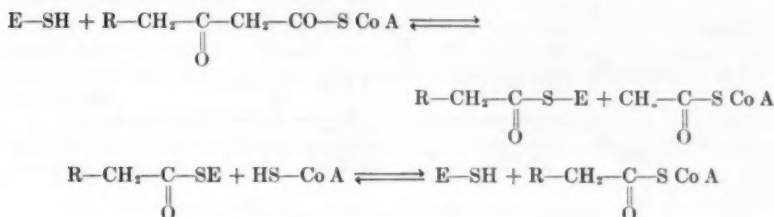
The reaction of hydroxyacyl-dehydrogenase (d) (Figure 4f) can be followed by measurement of the absorption at 303 m μ , the characteristic band of the enolate ion of any β -ketoacyl Co A⁷⁶.

The magnesium ion favors the formation of the enolate ion and shifts the equilibrium:



* In enzymology it is often convenient to designate a reactant by a letter (S = substratum, E = enzyme, etc.) and to separate symbolically the reactive function: S-H₂, E-SH, etc.

to the right. The specific hydrogen acceptor is diphosphopyridine nucleotide (DPN). According to Lynen and Ochoa⁷⁷, the active site of β -ketoacyl thiolase which catalyzes reaction (e) (Figure 4f) is a $-\text{SH}$ group and the scission-transfer reaction can be written:



2. Formation of acetoacetyl coenzyme A

Summary: Autocondensation of acetyl coenzyme A yields acetoacetyl coenzyme A. The latest advances in theoretical chemistry suggest the mechanism of this condensation:



The same enzyme as in reaction (5) (Figure 4e), the thiolase, leads to the following condensation:



The acyl-thiyl-S bond of acetyl Co A is of high chemical potential with the following free energy of hydrolysis:

$$\Delta F^\circ = -7.65 \text{ to } 8.25 \text{ kcal/mole}^{78}.$$

Such compounds, as well as those of ATP, ADP (with their phosphoanhydride bond) and acylphosphoanhydride of 1, 3-phosphoglycerate are physiologically important. They are thermodynamically less stable than their hydrolysis products. But under normal biological conditions of temperature and pH, they only react in presence of their specific enzymes. A paper by Lynen⁷⁹, dealing with the importance of acylthiyl-S compounds of coenzyme A, is recommended for further reading.

The state of polarization of the acyl-Co A molecule causes an increased ketone effect, an increased positive effect upon the carbon of the carboxyl group (Figure 4j).

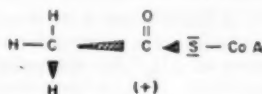


FIG. 4j.—Distribution of charges in the acetyl Co A molecule according to Lynen.

Evidence of this effect is given by spectrophotometric measurement of the absorption at 235 $\text{m}\mu$ ^{80, 79}.

Attacking the theoretical aspects of the problem, Pullmann⁸¹ has calculated the index of free valence and the bond index of different atoms and has given a mathematical picture of the phenomena. He confirms Lynen's conclusions (Figure 4k).

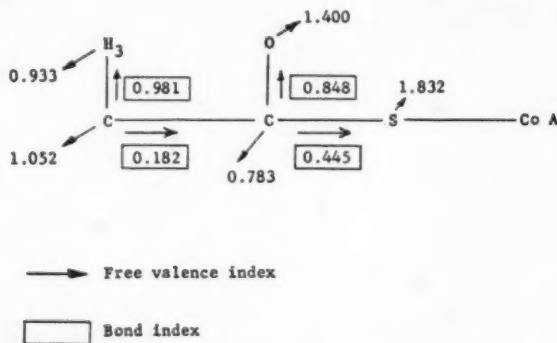
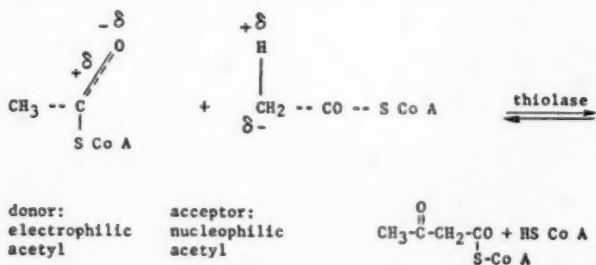


FIG. 4k.—Values of free valence and bond indexes of acetyl Co A, according to Pullmann.



It appears, that the carbon of the carboxyl group is strongly electron deficient, which explains its strong electropositivity, while the carbon of the methyl group has a slight excess of electrons. The reaction of the thiolase causes condensation of two molecules at the position of opposite electron density.

During the autocondensation of acetyl Co A, one molecule acts as acyl donor and is electrophilic, the other acts as acyl acceptor and is nucleophilic. This ambivalent character of acetyl Co A explains its position as turntable in glycolysis, the Krebs cycle and the metabolism of lipides.

The reaction equilibrium of the thiolase is predominately shifted to the left. Through spectrophotometric techniques (absorption at 303 mμ), it was possible to obtain the following values at pH 7 for the equilibrium constant and the free energy of the reaction:

$$K_{\text{eq.}} = \frac{(\text{acetoacetyl Co A})(\text{Co A})}{(\text{acetyl Co A})^2} = 1.6 \cdot 10^{-5}$$

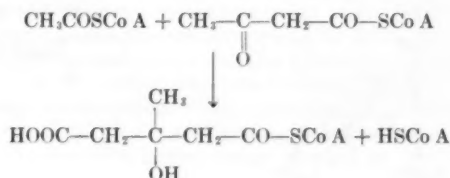
and $\Delta F^0 = + 6.600 \text{ cal/mole (28}^\circ \text{C)}$.

3. Formation of β -hydroxy β -methyl glutaryl coenzyme A

Summary: β -hydroxy β -methylglutaryl coenzyme A (HMG Co A) can originate either from condensation of one molecule of aceto acetyl Co A with a new molecule of acetyl Co A or from degradation of leucine.

The two ways of formation for HMG Co A are examples of "emergency metabolism" of the cell. Frequently, the cell can synthesize the same substance in several ways, as though to allow for the possible failure of one of the mechanisms.

a. Condensation of acetyl coenzyme A with acetoacetyl coenzyme A.—Under the influence of the condensation enzyme HMG Co A the reaction takes place according to the equation:



In order to prove that the condensation involves the thioesters and not the corresponding free acids, acetyl ^{14}C -Co A was incubated in presence of variable amounts of acetoacetic acid. No variations in radioactivity of the so formed HMG was observed. On the other hand, the presence of unmarked acetoacetyl Co A strongly increased the radioactivity of the soformed HMG (Table IV).

Yeasts, more active and more stable than liver preparations, are the best sources for this condensation enzyme.

Let us consider theoretically the bond indexes and the free valence indexes given by Pullmann⁸¹ for the acetoacetyl Co A molecule and for the acetyl Co A molecule (Figure 4l).

These diagrams show a strongly positive effect on the carbonylic carbon of acetoacetyl Co A and a strongly negative methylene carbon on acetyl Co A. This supports the classical pattern of the activation of the β -keto function.

The condensation product is HMG Co A, which implies the breaking of an acyl-thiyl-S bond. Rudnev⁸³ was first to show that the condensation

TABLE IV
EFFECT OF ACETOACETATE AND ACETOACETYL Co A UPON THE SYNTHESIS OF HMG
FROM ACETYL (1-¹⁴C) Co A IN EXTRACTS OF LIVER AND YEAST (RUDNEY¹²)

	cpm HMG		Yeast
	Rat liver	Beef liver	
(1- ¹⁴ C)Co A	4.000	375	5.400
(1- ¹⁴ C)Co A + 20 μ moles acetoacetic acid	—	—	5.700
(1- ¹⁴ C)Co A + 30 μ moles acetoacetic acid	4.100	—	—
(1- ¹⁴ C)Co A + 100 μ moles acetoacetic acid	4.000	—	—
(1- ¹⁴ C)Co A + 0.2 μ moles acetoacetyl co-enzyme A	—	1.875	20.000
	Exp. 1	Exp. 2	Exp. 3
	0.30 μ moles	0.30 μ moles	0.60 μ moles
	acetyl ¹⁴ C	acetyl Co A	acetyl ¹⁴ C
	Co A	¹⁴ C	Co A

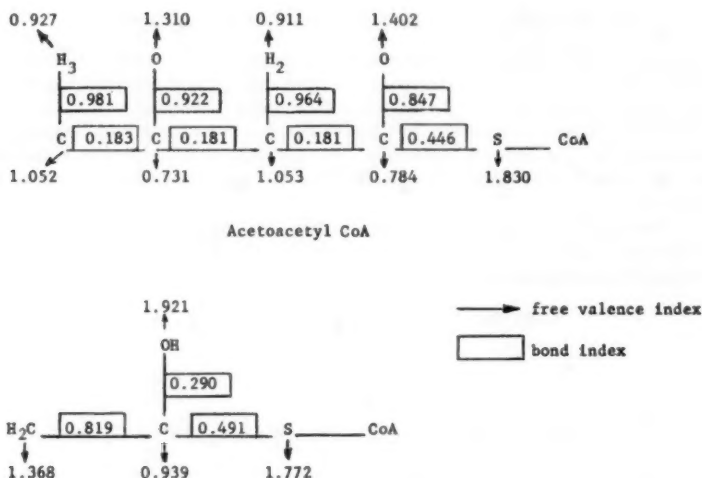


FIG. 4L.—Values of bond indexes and free valence indexes of acetyl Co A (enolic form) and of acetoacetyl Co A according to Pullmann.

product has the same R_f as HMG Co A synthesized chemically from HMG anhydride and coenzyme A.

Rudney⁸⁴ also proved that the hydrolyzed acyl Co A bond belongs to acetyl Co A. This was demonstrated by condensing acetyl 1^{14}C Co A with non-

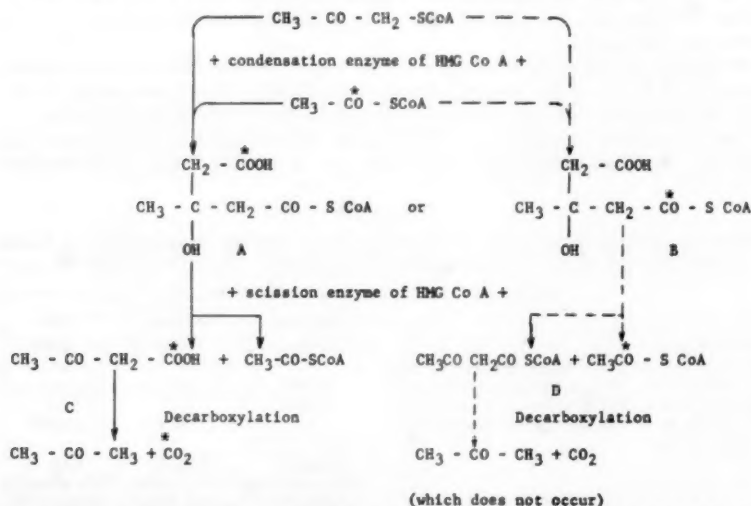


FIG. 4m.—Scheme suggested by Rudney's experiments. Hydrolysis of the acyl-thiyl-S bond of acetyl Co A during condensation with acetoacetyl Co A in presence of the condensation enzyme of HMG Co A.

marked acetoacetyl Co A. During this condensation, one molecule of coenzyme A is lost, but it is impossible to trace from what carrier it comes without marked molecules.

The resulting HMG Co A (cf Figure 4m) can be written in two ways, depending on whether coenzyme A is attached to the radioactive or the unmarked carboxyl group.

HMG Co A is then broken up by a specific enzyme into acetoacetic acid and acetyl Co A. Bond rupture occurs between the second and the third carbon atom next to coenzyme A. Depending on the position of coenzyme A, the radioactive product is acetoacetic acid or acetic acid. (Figure 4m, possibilities C or D).

Rudney decarboxylates acetoacetic acid with aniline and obtains marked carbon dioxide of radioactivity equivalent to the initial radioactivity of acetoacetic acid. Therefore, the free carboxyl group of HMG Co A is radioactive. The radioactivity of this group can only be due to the group ^{14}C of acetyl Co A. Rudney thus concludes, that the thioester group of acetyl Co A is hydrolyzed during condensation. The condensation reaction is practically irreversible in favor of HMG Co A. It is much less sensitive to iodoacetamide than thiolase. The variation in free energy at pH 7 is:

$$\Delta F^0 = -11.670 \text{ calories.}$$

The consecutive condensation without previous rupture of the molecules of acetyl Co A produces HMG—Co A. This was demonstrated by Rudney⁸² by incubating acetic acid ^{214}C with rat liver extract. He obtained the following isotopic distribution:

	cpm/m mole of CO_2
COOH	500
CH_2^*	11.100
CH_3^*	10.500
COH	250
CH_2^*	11.100
COOH	500

FIG. 4n.—Distribution of radioactivity in HMG synthesized from acetic acid ^{214}C .

Recently, Bücher, Overath and Lynen⁸⁵ have indicated that the condensation enzyme was essentially located in the mitochondria (rat liver). Preliminary treatment of the rat (tensioactive injection, young, etc. . .) does not interfere significantly with this localization of the enzyme.

b. Degradation of leucine.—This reaction sequence was actively studied by Coon's group and is summarized in Figure 40. Chichester and coworkers⁸⁶ have shown that *Phycomyces blakesleeanus* mildew can use leucine for the synthesis of carotene. They also reported⁸⁷ that leucine ^{14}C as well as leucine ^{214}C confers only little radioactivity to the hydrocarbon and therefore would provide only part of the C_5 condensation structure required.

Carbon dioxide and C_5 acids mutually stimulate their incorporation into cholesterol⁸⁸, which also suggests that the structures of C_5 acids are not directly incorporated.

For more than one reason, the decarboxylation (reaction (d) of Figure 4o) is of interest. It was described by Bachhawat and Coon⁸⁹. According to these authors, CO_2 first forms a compound with adenosine monophosphate

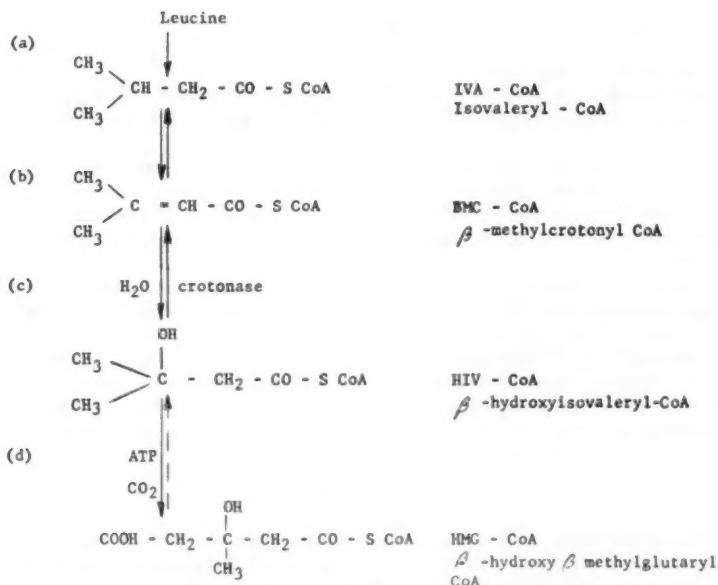
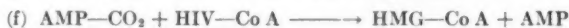


Fig. 4a.—Transformation of leucine to HMG Co A according to Coon and coworkers.

(AMP) produced from adenosine triphosphate (ATP). Liberation of pyrophosphate and decarboxylation of HIV—Co A produces HMG—Co A:



Reaction (e) is catalyzed by the CO_2 activation enzyme reaction (f) by the carboxylase of HIV—Co A. Woessner, Bachhawat and Coon³⁰ have specified that biotin bears an influence upon this carboxylation reaction. By measuring the amount of enzyme of the partial reactions (e) and (f) in liver extracts of normal rats and of rats with biotin deficiency, Coon's group³¹ concludes that biotin intervenes only in reaction (e) and not in reaction (f).

Chemically, it is difficult to consider the ester of β -hydroxy isovaleryl Co A as CO_2 acceptor. This would be a rare case of γ -carboxylation (Figure 4p) with protonization of one of the carbons:

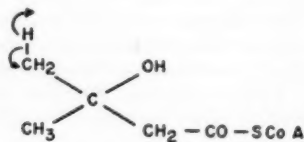


Fig. 4p.—Possibility of γ -carboxylation.

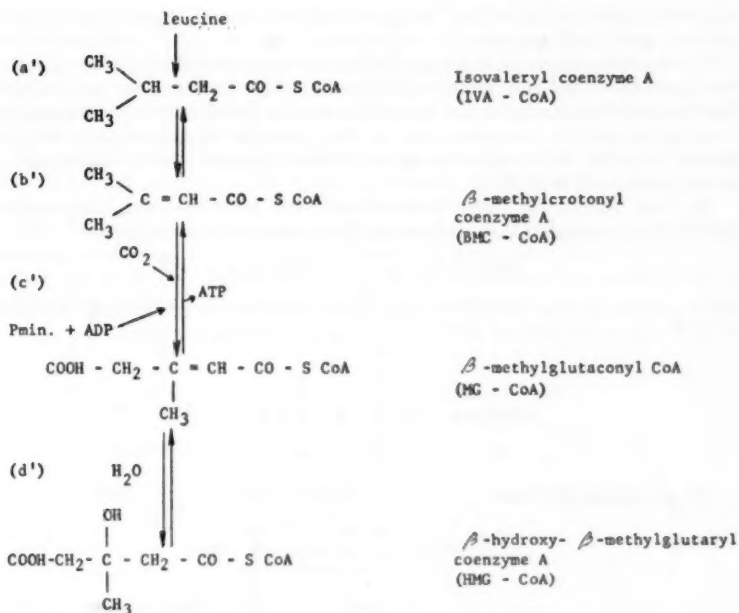


FIG. 4q.—Transformation of leucine to HMG Co A as suggested by Lynen.

Independently, Lynen's group⁹² has demonstrated with the enzyme isolated from *Mycobacterium* spp., that the true CO_2 acceptor is β -methyl crotonyl-Co A (BMC-Co A) and not HIV-Co A. This requires a revision of Figure 4o, because carboxylation occurs before hydration. The following reactions can then be written according to Figure 4q.

BMC—Co A carboxylase catalyzes reaction (c') (Figure 4q) and it contains biotin. Inhibition of the reaction by avidin can be countered by addition of biotin.

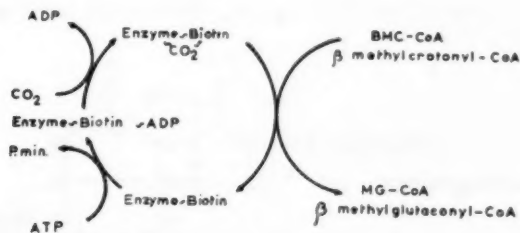


FIG. 4r.—Carboxylation of β -methyl crotonyl Co A according to Lynen.

β -Methylglutaconyl—Co A is then hydrated through action of a specific hydase: methyl glutaconase.

The reaction sequence in Figure 4q has now been accepted by Coon's group⁹¹ who has duplicated the earlier experiments with chicken liver preparations. This example demonstrates the interest as well as the difficulty of enzymology: a deduction can be erroneous due to the presence of a secondary enzyme. Special care has therefore to be taken, when organs or whole organisms are taken as a basis for study.

By first incubating these extractions with *p*-chloro-mercuribenzoate to inhibit the crotonase, Coon and coworkers suppressed the reaction:



which previously had interfered with their experiments when they attributed to HIV—Co A the role of BMC—Co A as acceptor of marked CO_2 .

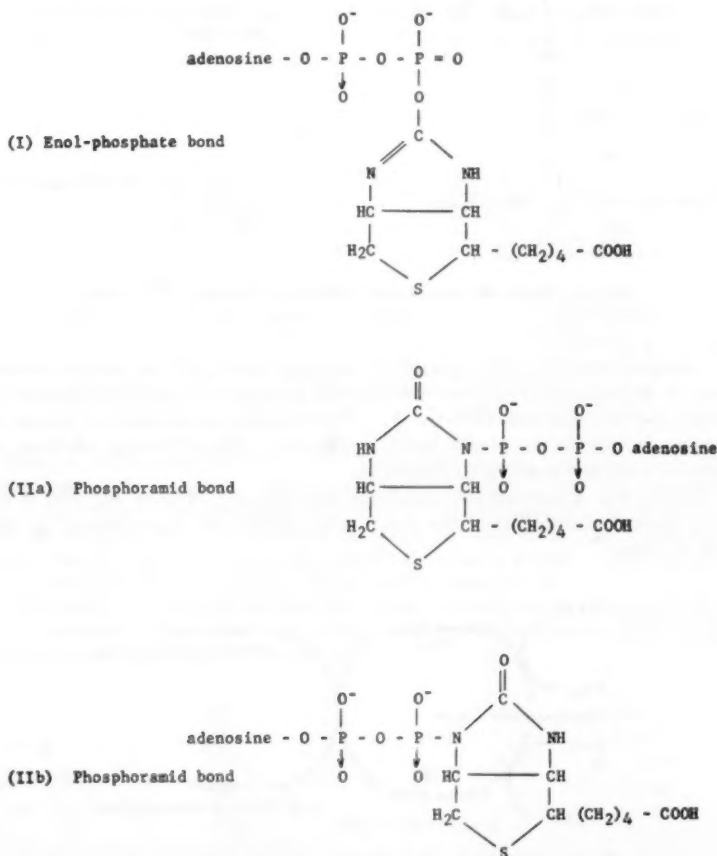


FIG. 4s.—Theory of Lynen concerning the adenosine triphosphate-biotin bond.

By isotopic exchange, Lynen and coworkers⁹² have analyzed the CO_2 activation mechanism. They propose the sequence indicated in Figure 4r.

BMC—Co A carboxylase (enzyme-biotin complex) forms a high potential combination with ADP, but the nature of the bond is not yet known [bond enolphosphate (I) or phosphoramidate (II), nor in this case, on what nitrogen atom (IIa or IIb) Figure 4s].

The combination enzyme—biotin—ADP reacts with CO_2 , liberating ADP, the high energy bond being transferred to CO_2 with formation of enzyme—biotin— CO_2 . (See however Kaziro et al.¹⁴³)

With $^{14}\text{CO}_2$, Lynen and coworkers⁹² succeeded in isolating a carboxylated derivative of biotin, which is very unstable in acidic medium, but stable at alkaline pH at 0°C . Therefore, as well as for other chemical reasons, one of the following configurations has been assigned (Figure 4t).

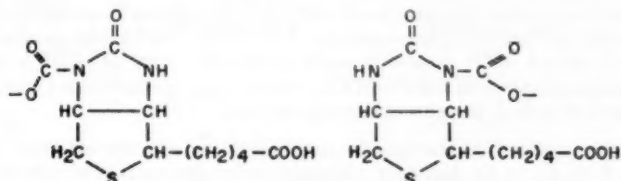
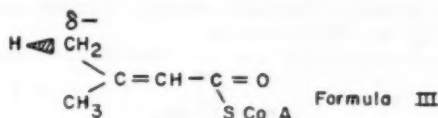


FIG. 4t.—Structures for the CO_2 -biotin complex.

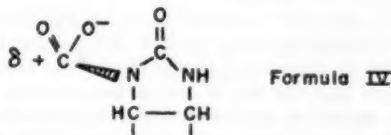
Thus, the carboxyl group would be linked to nitrogen and not to oxygen. Theoretically, the carboxylation of BMC—Co A can now be explained, because:

a) the $-\text{C}=\text{C}-$ double bond is in conjugation with the sulfur:



Polarization of the γ -carbon is favored and leaves a partial negative charge on this carbon atom.

b) the acid anhydride properties of the addition compound biotin— CO_2 result in the polarization of the $-\text{C}-\text{N}-$ bond toward the nitrogen:



The two metabolites therefore present structures which favor a transfer of the CO_2 group of IV to the carbon of BMC—Co A (III).

The transformation $\text{BMC}-\text{Co A} \rightarrow \text{HMG}-\text{Co A}$ is very important, because it explains the role of β -methylcrotonic acid as a precursor of rubber. This will be explained in the next section. This acid is a secondary metabolite which does not participate in the principal chain of reactions.

B. FORMATION OF "ACTIVE ISOPRENE"

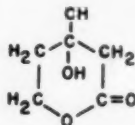
(Active isoprene designates the biologically active form of isoprene.)

Summary: The biosynthesis of terpenes and the principal metabolisms of fatty acids and amino acids have in common the primary formation of branched chain structures. $\text{HMG}-\text{Co A}$ can be recycled by scission into smaller molecules which undergo different reactions. $\text{HMG}-\text{Co A}$ is the last intermediate prior to the formation of specific compounds involved in the biosynthesis of terpenes. During the transformation of $\text{HMG}-\text{Co A}$ to MVA, the carboxyl group involved in the thioester bond with Co A is reduced to an alcohol group. This alcohol is then phosphorylated by ATP to 5P-MVA with production of ADP. A second ATP molecule reacts reversibly with 5P-MVA to give diphosphomevalonic acid (5PP-MVA), which loses one molecule CO_2 and one molecule H_2O to give isopentenyl pyrophosphate (IsPP).

It is remarkable that the terpene metabolism includes the esters of Co A in the step from C_2 to C_6 , but only phosphorylated derivatives of structures C_6 and C_8 in the following steps (Figure 4u).

1. Formation of mevalonic acid

The discovery of mevalonic acid (MVA) is due to the group of Folkers⁹⁵. In studying concentrated solutions of vitamin B_{12} , they isolated a new growth factor able to replace acetate for *Lactobacillus acidophilus* ATCC 4963. Identified as the lactone of β -hydroxy β -methyl δ -valeric acid, it was named mevalonic acid (MVA). Its formula is:



This acid is identical to hiochie acid previously isolated by Tamura⁹⁴.

In studying the metabolism of mevalonic acid, Tavormina and coworkers⁹⁶ were first to demonstrate that 43.4% of the radioactivity of the racemic $\text{dl}-2^{14}\text{C}-\text{MVA}$ is incorporated into cholesterol, versus only 3.8% from 4^{14}C BMC and 0.16% from 3^{14}C HMG.

Considering that only the "natural" form of the mixture is biologically active, the number obtained by using the 2^{14}C MVA indicates an incorporation of 86.8%. This yield by itself suggests the idea of the molecule being utilized without other changes than the loss of one carbon at most.

Despite this demonstration, numerous researchers have hesitated to consider mevalonic acid as biological precursor of terpenes. At the same time, the fundamental principle of biological carbon-carbon bond formation is based on condensations of the aldol or acyloin types which require at least one reactant to have an aldehyde or ketone function. These mechanisms are used often to

prolong or modify the carbon structure of substances and so to synthesize those compounds required by nature (hexose cycle, photosynthesis, etc. . .). But already the condensation of acetyl Co A with another molecule of acetyl Co A defies the rules. Also, it had not at that time been demonstrated that MVA could form from known precursors, such as acetyl Co A, acetoacetyl Co A, etc.

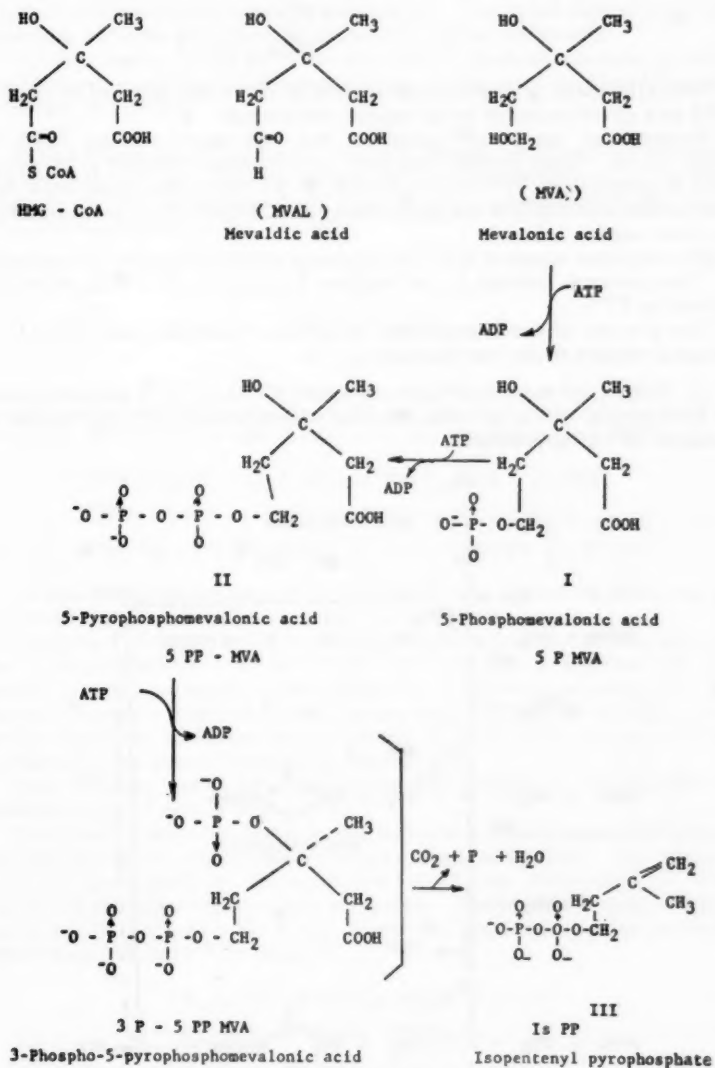
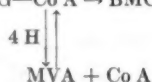


FIG. 4a.—Formation of "active isoprene."

The principle of the Claisen type condensation was so deeply anchored that MVA found in nature was rather considered as some form of reserve, which could regenerate β -methylcrotonyl-Co A (BMC-Co A) according to the equation:



Soon afterwards, increasing experimental evidence was supplied to confirm MVA as a direct precursor to all terpenic compounds.

Rudney and his group⁹⁶ presented the first paper relating MVA to HMG-Co A. They showed that after centrifugation (105,000 g) of bakers yeast in presence of TPNH₂ (or DPNH₂ + TPNH₂), the upper layer had incorporated about 50% of the radioactivity of ¹⁴C HMG-Co A in the resulting mevalonic acid.

The reduction occurs at the carboxyl group, which is esterified by coenzyme A. The process is endergonic and requires 2 molecules of TPNH₂ which are oxidized to TPN.

The question of the intermediate formation of mevaldic acid (MVAL) is discussed relative to the four findings:

(1) Wright and coworkers⁹⁷ have converted MVAL to MVA in an enzymatic rat liver system which, by preincubation with ribonuclease⁹⁸, was unable to transform MVA to cholesterol.

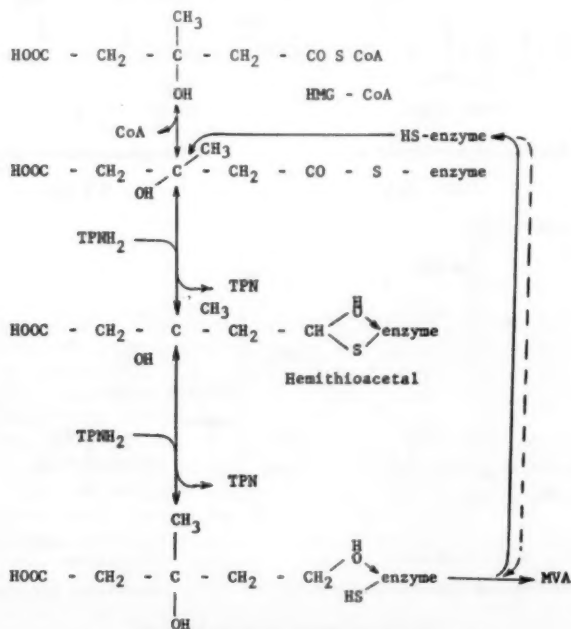


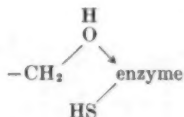
FIG. 4v.—Hypothetical reduction mechanism of HMG-Co A.

(2) MVAL added to an active liver homogenate is incorporated in the resulting cholesterol⁹³. This addition also lowers the incorporation of radioactivity from ^{14}C acetic acid into cholesterol.

(3) Various attempts to isolate mevaldic acid have failed. Knappe, Ringlemann and Lynen⁹⁹ have isolated and purified β -hydroxy β -methyl glutaryl reductase more than 350 times from yeast and showed that free mevaldic acid is not transformed by this enzyme. But in the case of enzymatic systems in animals, this intermediate can not yet be ruled out⁹⁵.

(4) Popjak and Cornforth¹⁰⁰ have proposed a hypothesis according to which the intermediate aldehyde derivative is joined to the enzyme by hemithioacetal formation (Figure 4v).

Such a theory would explain the failure to isolate MVAL during the reduction of HMG—Co A. Correspondingly, the low reversibility of the reaction⁹⁹ would be due to the last step of the transformation, particularly to the almost complete dissociation of the complex:



Although low, the reversibility of the reaction was proven⁹⁹ by coupling the formation of HMG—Co A with the action of the cleaving enzyme HMG—Co A:



As *p*-nitroaniline combines with the acetyl Co A formed its disappearance can be measured spectrophotometrically at $405 \text{ m}\mu$ ¹⁰¹.

Products with sulfhydryl groups such as cystein and glutathione stimulate the reaction $\text{HMG—Co A} \text{ ---} \rightarrow \text{MVA}$. This reaction is inhibited by iodoacetamid, which proves that the active site of the enzyme comprises —SH groups. Arsenate does not inhibit the reaction, but arsenite at high concentration causes an inhibition to the amount of 25%. Free coenzyme A also represses the reaction in the sense of reduction¹⁰².

Free HMG as well as its combinations with glutathione or pantethein are generally reduced very slowly.

If increasing doses of substratum are added to a definite amount of enzyme, the rate of reaction will increase until a maximum is reached. The Michaelis constant (mole/liter) is the concentration of the substratum at which half of the maximum reaction rate is reached. The Michaelis constant of the reaction $\text{HMG—Co A} \rightarrow \text{MVA}$ was determined graphically by the method of Lineweaver and Burk¹⁰³ by Knapp⁹⁹:

$$K_m = 1.5 \cdot 10^{-6} \text{ (mole HMG—Co A/l)}$$

$$K_m = 8 \cdot 10^{-5} \text{ (mole TPNH}_2\text{/l)}$$

the optimum pH for the reaction is 6.5.

Thus, it was proven that the oxidation-reduction $\text{HMG-Co A} \rightarrow \text{MVA}$ is an enzymatic reaction.

Witting and Porter¹⁰⁴ have recently incubated a liver homogenate with marked acetic acid in presence of nonradioactive MVA and isolated and characterized radioactive MVA formed from acetic acid. There is no doubt as to the transformation of acetic acid to MVA.

The question remains as to the incorporation into terpenes of a substance like MVA, having no active groups (aldehyde or ketone) and no activator (Co A).

A series of ingenious experiments was carried out by Bloch's school^{105, 106} which made a fundamental contribution to the understanding of the incorporation mechanism of mevalonic acid into terpenes.

It was known, that the carboxyl group of MVA is lost during the synthesis, therefore the two carbons producing a head to tail bond are in positions 2 and 5 of MVA (Figure 4w).

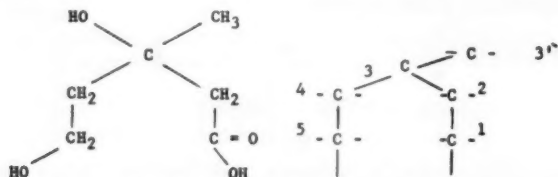


FIG. 4w.—Numbering of carbons in MVA.

Bloch and his coworkers have marked MVA not only with ^{14}C but also with deuterium and tritium and have prepared $2^{14}\text{C}_5\text{D}_2\text{MVA}$ and $2^{14}\text{C}_5\text{T}_2\text{MVA}$. It then became possible to follow the degree of oxidation of carbons 2 and 5 by evaluating the gain or loss of hydrogen atoms attached to these key positions. The experiment proved the degree of oxidation of carbons 2 and 5 to be unchanged. This result suggested to the authors that the carbon-carbon bond established between two molecules of MVA was created by an unusual biological reaction, since it involved a coupling of two active methylene groups. From this and from similar experiments carried out in presence of D_2O it is possible to deduce:

(1) Since the oxidation level of carbon 5 stays the same during condensation of MVA, neither mevaldic acid nor HMG-Co A can act as intermediate between the formation of MVA and that of squalene.

(2) The loss of CO_2 does not occur before or after the condensation, otherwise deuterium would incorporate into the squalene molecule when the condensation is carried out in presence of D_2O .

Bloch believes that the condensation and the decarboxylation are coupled processes.

Only part of this theory is verified, because Bloch and his coworkers found later, that decarboxylation occurred together with a dehydration to form isopentenyl pyrophosphate.

2. Formation of 5-phosphomevalonic and 5-pyrophosphomevalonic acid

It was obvious, that ATP is indispensable to the transformation of MVA. After elimination of a possible activation by coenzyme A or by ketone functions, one turned towards the phosphate esters.

In 1957, Tchen¹⁰⁷ was first to describe MVA-kinase, isolated and partially purified from an autolysis product of yeast. This enzyme assures the primary phosphorylation of MVA.

The identity of the reaction product with 5PMVA was first determined from the following considerations:

Starting from ^{14}C MVA, a radioactive product was found indicating that the carboxyl group was not lost.

By using ATP marked with ^{32}P in both terminal P groups the reaction product contains proportions of MVA/ ^{32}P equal to 1/1. Indeed, the possible formation of a complex MVA—ADP must be eliminated, because the product has no chromophoric group. The MVA-phosphate bond is not of an acyl-phosphate nature, since it is resistant to acids and bases and does not react with hydroxylamine. It is therefore a phosphate ester of MVA. Based on chemical considerations, it can be predicted, that the ester bond will be on carbon 5. (Figure 4x).

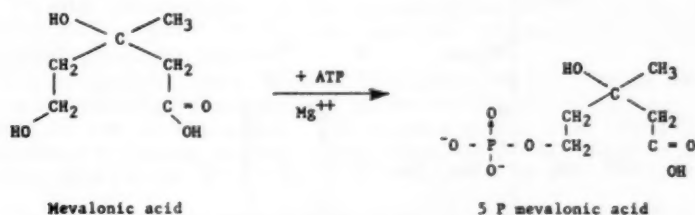


FIG. 4x.—Formation of 5 phosphomevalonic acid.

Comparison with a synthesized derivative^{93, 108, 109} confirmed the position of the phosphate group attached to the hydroxyl group on carbon 5. Popjak and coworkers^{110, 111} have isolated and partially purified from pork liver extracts an MVA-kinase with high specific activity, 700 μg (5.4 μmoles) MVA/mg protein/hr at 37° C.

$$K_m = 5.0 \cdot 10^{-5} \text{ moles/MVA/l}^{112}$$

The reaction consumes one molecule ATP per molecule of PMVA formed and requires the presence of a divalent ion (Mg^{++} , Mn^{++} , . . .). ATP can be replaced by guanosine triphosphate (GTP), cytidine triphosphate (CTP), or uridine triphosphate (UTP). The reaction is inhibited by *p*-chloromercurobenzoate. The optimum pH of the reaction (yeast) is between 6.4–6.7. The kinase is specific with respect to the stereochemical form of the substratum and catalyzes only the phosphorylation of the enantiomorph which is the "natural" form.

The incorporation of 5PMVA into terpenes also requires the presence of ATP. By using ^{32}P and ^{14}C (AT^{32}P and $5^{32}\text{P}\text{MVA}2^{14}\text{C}$), Bloch and coworkers¹¹³ have in effect demonstrated that:

(1) the reaction consumes one molecule of ATP per molecule of 5PMVA metabolized.

(2) the product formed still contains 6C atoms, thus the carboxyl group has not yet been eliminated.

(3) the product contains a proportion of $^{32}\text{P}/^{14}\text{C}=2$; the product formed is therefore a diphosphomevalonate. The latter is characterized by a greater

polarity than PMVA (smaller R_F on paper, greater retention on ion exchange columns Dowex-1 formate).

The bond of the two phosphates is stable in alkaline pH. In acidic pH, a scission product identical to 5PMVA is obtained. Since it is difficult to suppose a stable tertiary phosphoric ester, the resulting diphosphate is presumably 5 pyrophosphomevalonic acid (Figure 4y).

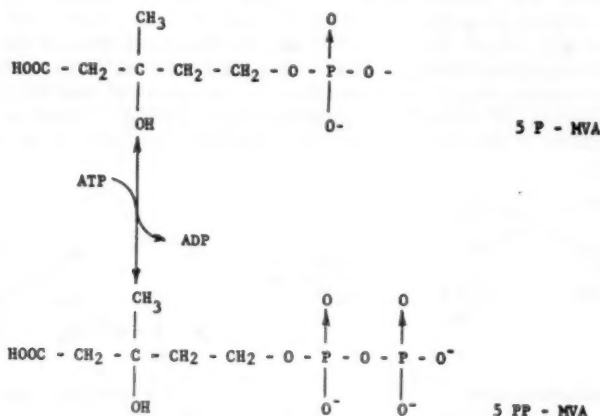


FIG. 4y.—Formation of 5 pyrophosphomevalonic acid.

The reaction is catalyzed by an enzyme different from MVA kinase and requires the presence of Mg^{++} . If the enzymatic system does not present any great activity in ATP-ase, DPNH-oxidase, etc. . . , then the reaction can be followed by using Lynen's¹⁰⁸ technique, by coupling the action of kinase (reaction a) with that of pyruvic kinase (reaction b) and the lactic dehydrogenase (reaction c) (Figure 4z).

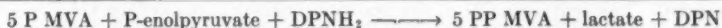
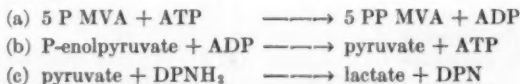


FIG. 4z.—Details of the reaction $5 \text{ P MVA} \longrightarrow 5 \text{ PP MVA}$.

Henning and coworkers¹¹⁴ showed this phosphorylation to be reversible. There is no optimum pH, because the activity remains practically constant over a large pH range (5.5–10.0). The optimum concentration of ATP is 0.01M; at higher concentration, inhibition will occur.

5PMVA kinase though not crystalline but prepared from purified pork liver extract (Hellig and Popjak quoted in Popjak and Cornforth¹⁰⁰) shows a similar activity (4.5 μ moles phosphorylated 5PMVA/mg protein/hr at 37° C) but differs from 5PMVA kinase isolated from yeast because it requires an optimum pH of 7.4 and the presence of cystein in aerobic medium.

These authors have also confirmed the reversibility of the reaction, since phosphorylation is complete only if ADP is eliminated from the reaction, becoming ATP by coupling with pyruvic kinase and lactic dehydrogenase. The Michaelis constant of this reaction is:

$$K_m = 3.0 \cdot 10^{-14} \text{ moles 5PMVA/l}^{112}$$

3. Formation of isopentenyl pyrophosphate

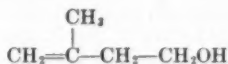
The further transformation of 5PPMVA still requires ATP and the latter can not be replaced by either ADP or AMP.

Using the same isotope technique as before, Bloch and coworkers¹¹³ could characterize the product of the next step, the compound III (Figure 4u) as follows:

(1) after determination of the proportion of $^{14}\text{C}/^{32}\text{P}$ in incubated $^{32}\text{PPMVA}2^{14}\text{C} + \text{ATP}^{32}\text{P}$, it was concluded that compound III contains 2 phosphate groups per molecule.

(2) during incubation of $5\text{PMVA}1^{14}\text{C}$ in presence of ATP in the fraction of yeast containing "decarboxylase," radioactive CO_2 was released and compound III was not radioactive. The reverse was true, when $5\text{PPMVA}2^{14}\text{C}$ was chosen as starting material. Thus, compound III is a decarboxylation product of 5PPMVA.

In order to identify its carbon structure, Bloch and coworkers¹¹³ treated compound III with phosphatase of cobra venom, which liberated a volatile and radioactive alcohol. This alcohol was purified by gas chromatography and the 3,5-dinitrobenzoate prepared. This analysis identified the alcohol as 3-methyl-3-butenol or isopentenol:



This identity was confirmed later by comparison with chemically synthesized isopentenyl pyrophosphate. Both substances behave similarly from the physical chemical as well as from the enzymatic point of view (Lynen and coworkers¹¹⁵, Yuan and Bloch¹¹⁶, Eggerer and Lynen¹¹⁷).

Since there is only one alcohol function, Compound III will be the isopentenyl pyrophosphate. The passage from PPMVA to IsPP takes place by decarboxylation and loss of the tertiary hydroxyl group on C3. Since ATP is necessary, an intermediate phosphorylation step appears also necessary. The triphosphorylated intermediate has never been isolated, either because of its instability or because of the formation of a complex enzyme-substratum.

On the basis of their experiments, Bloch and coworkers¹¹³ consider the decarboxylation and dehydration processes (or de-esterification of the hypothetical tertiary phosphate) as being synchronized. This idea is supported by the fact, that IsPP formed in T_2O containing water does not contain any tritium. The reaction mechanism is indicated in Figure 4aa.

No proton formation occurs on the carbon chain. This mechanism of concerted decarboxylation and dehydration of a β -hydroxy acid to an olefin with terminal double bond is without equivalent in biochemistry. Only chemical

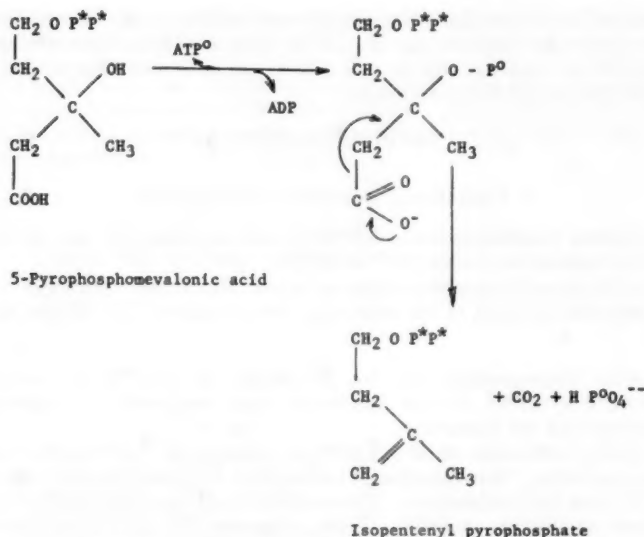


FIG. 4as.—Concerted mechanisms of the reaction of the "decarboxylase" (Bloch and coworkers¹¹³).

analogies can be found: transformation of dibromo cinnamic acid to β -bromo styrene or of β -isovalerolactone to isobutylene¹¹³.

Popjak and Cornforth¹⁰⁰ have proposed the name of "5 di P MVA anhydro decarboxylase" for the enzyme which catalyzes the transformation of 5 PP MVA to IsPP. The reaction requires an optimum pH between 5.5 and 7.4. The magnesium ion can be replaced by Mn^{++} , Fe^{++} , Zn^{++} or Co^{++} at concentrations between 0.001 and 0.01 *M*. The purified enzyme has an activity value¹¹³ of:

$$40 \mu\text{moles 5 PP MVA/mg protein/hr}$$

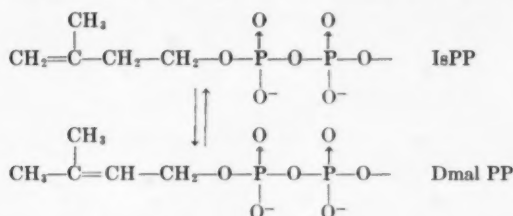
C. INITIATION

Summary: The initial condensation of isopentenyl pyrophosphate can only occur in presence of an initiator, that is, a molecule of appropriate structure. This initiator is produced by isomerization of isopentenyl pyrophosphate to dimethylallyl pyrophosphate.

Formation of dimethylallyl pyrophosphate.—In analogy to chemical polymerization reactions, this step is called initiation. Isopentenyl pyrophosphate is considered to be the monomeric building block. It will be seen later, that this terminology corresponds in fact to a starting signal for the enzymatic process.

The previously described studies show IsPP to have a terminal double bond. Isomerization of IsPP at a certain moment has to be considered, since squalene has two methyl groups in terminal positions. This step takes place previous to condensation, since the farnesyl pyrophosphate, which will be mentioned

later, is an intermediate in the formation of squalene from MVA¹¹⁵ and since the farnesyl group already has two terminal methyl groups. Recently, Agranoff and coworkers^{118, 119} have isolated IsPP isomerase. It catalyzes the isomerization of isopentenyl pyrophosphate (IsPP) to dimethylallyl pyrophosphate:



The same authors have purified this enzyme 20 times starting from an autolysis product of yeast. The activity of such a system was found to be equal to 1 μ mole of IsPP/mg protein/hr at 37° C. Subsequent treatment comprising a light alkalization over a short time, yields an enzyme, which is purified about 6 times and is much more active:

6.55 μ moles substratum/mg protein/hr at 37° C

The reaction is an equilibrium. The incubation of a mixture of synthetic Dmal PP and isomerase in presence of tritium containing water results in a product, which, after hydrolysis by phosphatase yields radioactive isopentenol. Although the exact proportions of the two isomers can not be established accurately, the equilibrium is strongly shifted in favor of Dmal PP formation (about 93%).

The isomerization reaction requires the presence of Mg^{++} ion at a concentration below 6 μ moles/ml, otherwise the Mg^{++} ion will act as an inhibitor. The Michaelis constant of this reaction is:

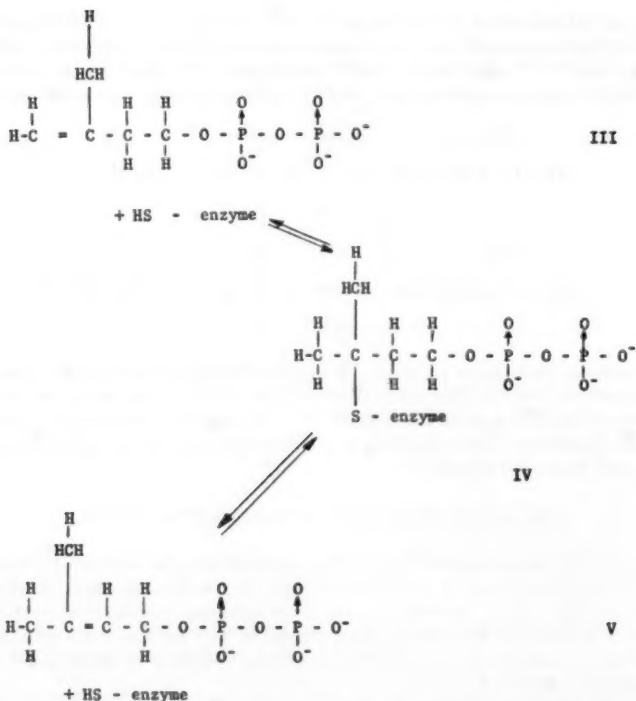
$$K_m = 3.6 \cdot 10^{-5} \text{ M/l}$$

The reaction is inhibited by: 10^{-4} M of para chloromercuribenzoate, 10^{-3} M of iodoacetamide.

Addition of reduced glutathione partially suspends the inhibition caused by *p*-chloromercuribenzoate. The isomerization product of IsPP is identical with synthetic dimethylallyl pyrophosphate. Contrary to isopentenyl pyrophosphate, the pyrophosphate bond of the allylic isomer is very labile. Acidic hydrolysis causes an allylic rearrangement which produces dimethylvinylcarbinol.

It will be seen later, that IsPP condenses with Dmal PP to produce geranyl PP. This condensation can be compared to the formation of fructose-1, 6-diphosphate which is preceded by isomerization of triose phosphate (dihydroxyacetone phosphate) to its isomer (phosphoglyceraldehyde) which facilitates condensation.

Because of its sensitivity to *p*-chloromercuribenzoate and to iodoacetamide, IsPP-isomerase is an enzyme containing —SH groups. On the basis of analogy with the Willgerodt reaction and by isotopic exchange in tritium containing water, Agranoff and coworkers^{118, 119} could establish the mechanism of IsPP isomerase action (Figure 4ab).

FIG. 4ab.—Mechanism of isomerization of IsPP (Agranoff and coworkers¹¹⁹).

The enzyme (E—SH) forms a saturated addition product (IV) which, in decomposition, resembles the starting product (III) as well as the Dmal PP (V) (Figure 4ab).

D. CONDENSATION OF ISOPRENE UNITS

Summary: The condensation of isoprene units can occur either head-to-tail or tail-to-tail. The first mechanism will produce geranyl pyrophosphate, then farnesyl pyrophosphate and finally polyisoprene. The formation of squalene to the contrary is the result of a tail-to-tail condensation mechanism.

With better than human skill, nature makes use of head-to-tail and tail-to-tail polycondensations to form the various terpenes. The question is to know, which mechanisms induce one or the other chain from the same starting materials. At this point, the biosynthesis of terpenes diverges to produce the whole variety of terpenes, among which we find polyisoprene.

1. Head-to-tail condensation mechanism

a. Formation of geranyl pyrophosphate.—The condensation of IsPP with Dmal PP produces geranyl pyrophosphate (GePP), with liberation of mineral phosphate (P min.) (Figure 4ac).

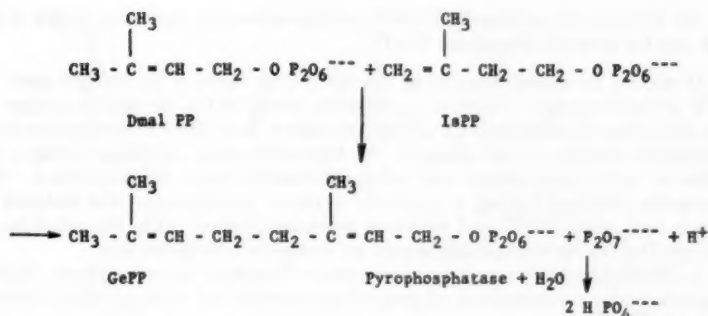


Fig. 4ac.—Formation of geranyl pyrophosphate.

An inorganic orthophosphate is formed, since the enzymatic system, even after 20 purifications, still contains some pyrophosphatase.

The reaction requires the presence of magnesium ion. It is unknown, whether the enzyme inducing this condensation is identical to the enzyme inducing the condensation of GePP and IsPP to form farnesyl pyrophosphate (Fa PP). It is still uncertain, if several specific synthetases exist for carbon chains, of different length. Nobody has yet answered this question, but it appears that the condensation is not a concerted process, since the different intermediates have been isolated.

It is believed, that the pyrophosphate bond which is hydrolyzed during condensation, belongs to dimethyl allyl pyrophosphate, thus producing a carbonium ion (VI) which would react with the double bond of isopentenyl pyrophosphate under loss of a proton according to the sequence of Lynen and coworkers¹²⁰ (Figure 4ad).

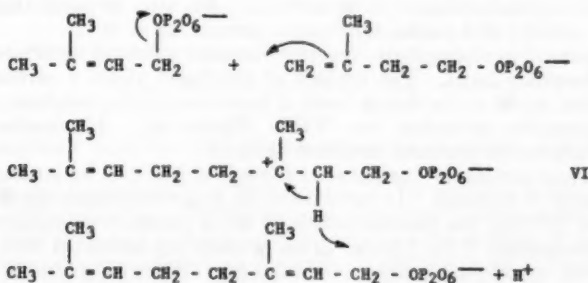


Fig. 4ad.—Formation mechanism of geranyl pyrophosphate.

The identification of GePP as an intermediate in the biosynthesis of terpenes was established by the Lynen¹²⁰ group and involves

(1) By working with a large excess of Dmal PP in the presence of synthetase, IsPP, and iodoacetamide to block the action of isomerase, geraniol was found by hydrolysis and was identified by electrophoresis and crystallization of its *p*-nitroazobenzoic ester, m. 101–2° C.

(2) Chemically synthesized GePP incorporates into squalene, which is not the case for geranyl phosphate (GeP).

It should be noted, that after the IsPP step there is no further need for ATP in condensation. There is a question, whether the energy necessary for the alkylation is furnished by allylic resonance alone or by the hydrolysis of phosphoric bonds of high energy. In the latter case, coupling between the action of pyrophosphatases and of synthetase(s) must be considered. The enzymatic fraction having a synthetic activity (synthetase) was isolated by Lynen and coworkers¹²⁰ and contains pyrophosphatase. On the other hand, the reaction seems irreversible, based on energetic considerations.

b. Formation of farnesyl pyrophosphate.—Farnesyl pyrophosphate (FaPP) is produced by condensation of geranyl pyrophosphate with another molecule of IsPP (Figure 4ae).

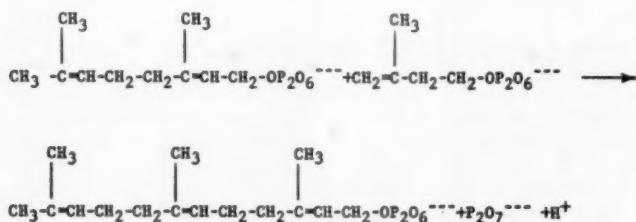


FIG. 4ae.—Formation of farnesyl pyrophosphate.

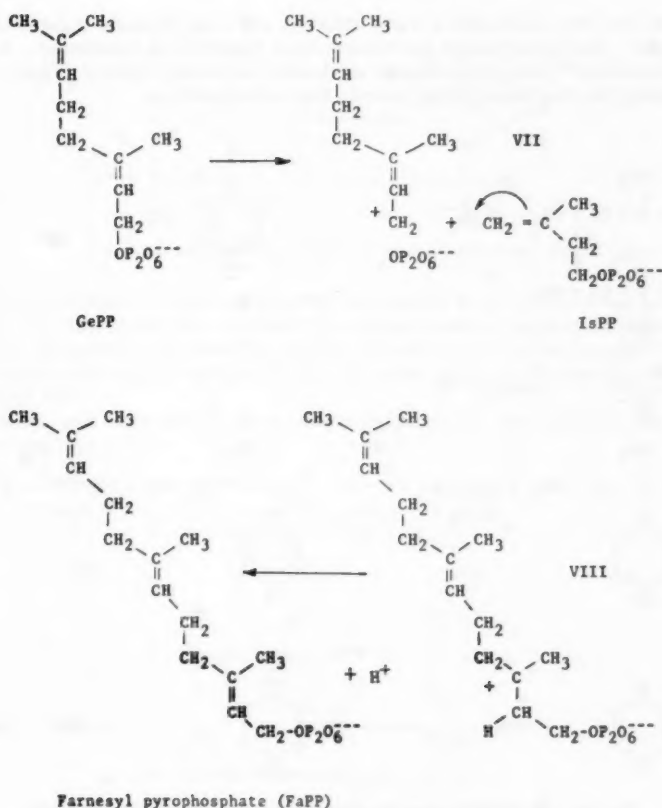
Lynen and coworkers¹¹⁸ had identified FaPP before having isolated GePP and this guided their search for GePP. The reaction also requires the presence of magnesium ion and follows a mechanism identical to the preceding condensation. By complexing this ion, diaminetetracetic acid inhibits the reaction.

Farnesyl-pyrophosphate-synthetase from yeast, after 20 purifications shows a specific activity of 4 μ moles IsPP/mg of protein/hr at 37° C.

The geranyl pyrophosphate structure contains an allylic structure relative to the phosphate bond. The rupture of this bond yields a carbonium ion (VII) which, added to the double bond of isopentenyl pyrophosphate, produces another unstable carbonium ion (VIII) (Figure 4af). Elimination of one proton produces the stabilized structure of FaPP.

Lynen and coworkers¹¹⁸ established the role of FaPP as an intermediate in the synthesis of squalene. In presence of an active enzymatic system and in absence of TPNH₂, the transformation of MVA produces no squalene, but a product designated Y by Lynen. This product was extracted with collidine and purified by chromatography over silica gel. When incubated in presence of TPNH₂, the purified product was converted to squalene.

Product Y is very sensitive to acids. From substrata marked with ³²P and ¹⁴C, Lynen and coworkers¹¹⁸ could identify the hydrolysis products. On paper chromatography, the spots corresponding to pyrophosphate as well as to farnesol were radioactive. Synthetic farnesol was used as a carrier. The identity of product Y with farnesol was also demonstrated by its *p*-nitroazobenzoic ester (m. p. 86–88° C), by the reduction to farnesyl and crystallization of the corresponding semicarbazone and by ozonolysis. In addition, synthetic FaPP is also transformed to squalene.

FIG. 4a_f.—Formation mechanism of farnesyl pyrophosphate.

C. SUBSEQUENT HEAD-TO-TAIL CONDENSATION OF FARNESYL PYROPHOSPHATE

Little direct experimental evidence exists for the condensation of FaPP with a new IsPP molecule. But Lynen and coworkers¹²⁰ have mentioned, that during their work with a crude enzymatic fraction from yeast, they succeeded in isolating a phosphorylated geranyl geraniol derivative which was very labile in an acidic medium.

The mechanism of this reaction would be identical to those described earlier: condensation of IsPP with an allyl pyrophosphate, etc. . . .

2. Tail-to-tail condensation mechanism

The explanation for the synthesis of squalene from FaPP or of carotene from geranyl geraniol pyrophosphate is based on a tail-to-tail condensation of two molecules of those intermediates. But this condensation without modifica-

tion of the two molecules is very unlikely, since an opposite polarization is required. An isomerization mechanism must therefore be considered. Lynen and coworkers¹²⁰ propose an elegant mechanism involving a quinol (Figure 4ag), in analogy to reactions taking place in the mitochondria.

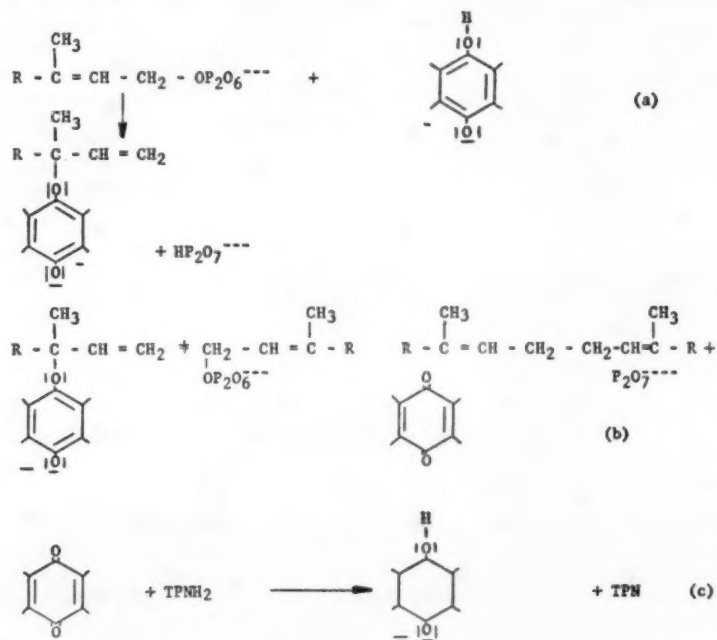


FIG. 4ag.—Hypothetical mechanism of squalene formation from FaPP according to Lynen and coworkers.

After allylic isomerization, a first FaPP molecule combines with quinol to form a nerolidyl ether (reaction a). This derivative presents a terminal double bond and can react with carbonium formed by rupture of the pyrophosphate bond of a second FaPP molecule in order to yield squalene and liberate quinone and pyrophosphate (Reaction b). Quinone would then be reduced to quinol by TPNH_2 (Reaction c) and be recycled.

In the course of their work with enzymatic liver systems, Popjak and coworkers^{121, 122} treated some reaction products extracted with collidine to the hydrolyzing action of snake venom at pH 8.3. They obtained neutral, ether soluble products. Gas-liquid radiochromatography revealed, among other substances, the presence of *trans*-nerolidol in amounts of about $\frac{1}{2}$ of that of *trans-trans* farnesol. They believe the initial derivatives of nerolidol to be pyrophosphates, formed by action of an isomerase predicted by Cornforth and Popjak. This theory differs somewhat from the one proposed by Lynen (see p. 1281). The isomerization could take place by rearrangement of the pyrophosphoric groups according to Figure 4ah:

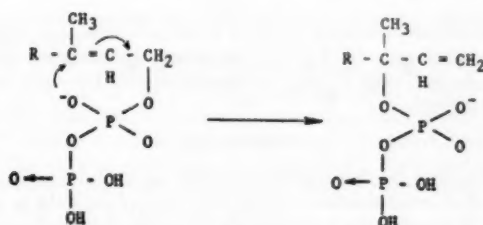
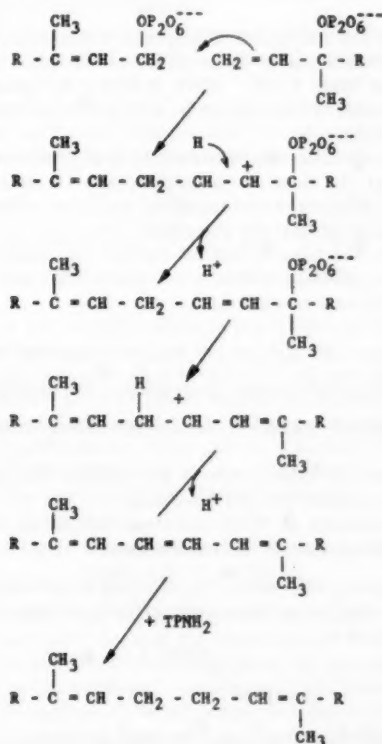


FIG. 4ah.—Isomerization of FaPP according to Cornforth and Popjak.

The mechanism of electrophilic attack is similar to the head-to-tail condensation: the condensation is initiated by rupture of the pyrophosphate bond of farnesyl pyrophosphate, resulting in the formation of a carbonium ion. The subsequent electrophilic attack of this ion takes place at the double bond of nerolidol PP.

Popjak and coworkers¹²² have therefore proposed the following reaction sequence (Figure 4ai):

FIG. 4ai.—Coupling mechanism of C₁₅ structures (Popjak¹²²).

The first stable condensation product is dehydrosqualene, directly reduced by TPNH_2 to squalene. In Lynen's sequence, the degrees of oxidation of C_{15} compounds do not vary during condensation and the only role of TPNH_2 is to regenerate quinol.

E. TERMINATION

The chain stopping mechanisms in isoprenic polycondensation have not yet been studied. Autocondensation of farnesyl pyrophosphate is a termination mechanism, but it is not likely to terminate the polycondensation of isopentenyl pyrophosphate in the biosynthesis of rubber.

On the basis of today's knowledge, it is possible to consider the increasing stabilization by resonance of the growing chain and at the same time the decreasing activation of the pyrophosphate bond. The molecular structure would then finally become unable to add new isoprenic units. In this case, the terminal isoprenic unit should carry a phosphorylated alcohol function.

Deactivation could also occur by simple dephosphorylation. Experimental evidence³² shows in fact, that isopentenyl monophosphate or geranyl monophosphate can no longer be metabolized. But none of these three theories, tail-to-tail condensation, inactivation by resonance or dephosphorylation is really convincing.

All fail to explain the formation of important chains in the case of rubber. Inactivation by resonance starts to be effective for molecular weights of the order of $1 \cdot 10^6$ rather than $1 \cdot 10^5$. Also, it is hardly possible, that dephosphorylation or tail-to-tail condensation be accidental and limited to molecules of high molecular weight.

The problem of molecular weight of rubber is of great interest, because if it could be controlled at the time of *cis*-polyisoprene formation, natural rubber would acquire highly important technological qualities, either by limitation or extension of the number of units in the chain.

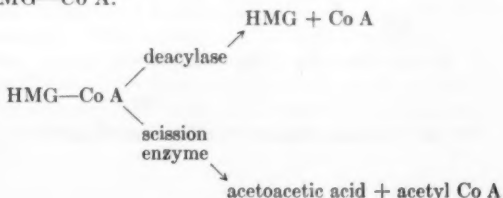
Within five years, the biosynthesis of rubber has made extraordinary advances. At this pace, perhaps within a few years from now, this problem will be solved, utopic as it may now seem.

F. CONTROL AND REGULATION OF THE METABOLISM OF TERPENES

In the general scheme of terpene biosynthesis, we distinguish:

1. *step*: Formation of branched carbon structures from acetyl Co A to HMG—Co A.
2. *step*: Reduction of HMG—Co A to MVA. The reduction requires 2 TPNH_2 per molecule of MVA formed.
3. *step*: Phosphorylation of MVA and decarboxylation of 5 PP MVA.
4. *step*: Polycondensation of "active isoprene".

The first step can be halted either by decrease in activity of thiolase which assures the condensation, or by increase in activity of deacylases or of scission enzyme of HMG—Co A.



This latter enzyme is particularly active in mitochondrias of the liver (Bücher and coworkers⁸⁵).

Furthermore, HMG deprived of coenzyme A is an antimetabolite for the transformation of MVA by the *Lactobacillus acidophilus* 4963¹²³.

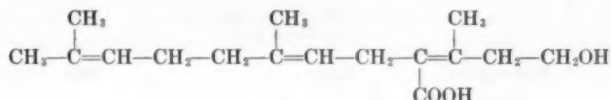
The second step has drawn particular attention from researchers. Bücher and coworkers⁸⁶ believe the activity of HMG—Co A reductase to have a great influence upon the rate of synthesis of cholesterol. Rats under a severe diet before the experiment itself, show a lower cholesterol formation without lesser formation of HMG—Co A and acetoacetate.

Since this second step requires the presence of TPNH₂, Siperstein and Fagan¹²⁴ rather believe that the proportion of this reducing agent conditions the cholesterol synthesis, since it is accelerated by incubation in presence of glucose 6—P and TPN but is not influenced by DPN or DPN + TPN alone. The degradation of glucose 6—P partially assures the regeneration of TPNH₂ from TPN.

In the third step—phosphorylation of MVA and decarboxylation of 5 PP MVA—Levy and Popjak¹¹¹ have noted that farnesoic acid acts as inhibitor on MVA-kinase. They suggest that this action could constitute a physiological control mechanism for the sterol synthesis in mammals. Wright and Cleland⁹⁸ and Wright¹²⁵ also noted this inhibition.

FaPP for example could produce farnesoic acid by oxidative dephosphorylation. This would be a case of "feed-back control" by deviation of a metabolism as a result of action upon a former step. Other homologs of farnesoic acid (geranoic acid, geranyl geranoic acid) were also noted as inhibitors.

Ogilvie and Langdon¹²⁶ have isolated and identified a C₁₆ olefinic acid after incubation of a liver homogenate with mevalonic acid 2¹⁴C.



Its significance in the terpene metabolism is still unknown, but could be similar to that of farnesoic acid.

After incubation in vitro of sodium acetate 2¹⁴C in latex of *hevea brasiliensis*, Fournier and coworkers²⁶ have found formation of labelled malonic acid or of its Co A ester. These authors found, that the yield of transformation of sodium acetate based on the radioactivity of the rubber is higher, the lower the malonic acid formation. It is therefore conceivable, that the presence of this acid is related to a control mechanism of the rubber synthesis.

V. BIOSYNTHESIS OF *cis*-POLYISOPRENE, A PARTICULAR CASE OF TERPENES

The preceding section summarizes the essentials of the published work on the mechanism of the biosynthesis of the terpenes and related products as well as the modern theories which they have produced (cf. general scheme, Figure 1a, page 1232). It has yet to be shown in grouping the information reported in the literature, that the formation of *cis*-polyisoprene follows the same pattern.

This information concerns only certain particular points, but the fragmentary observations prove the similarity of the mode of formation of all terpenic substances, including polyisoprene.

A. EVIDENCE FOR THE FUNCTION OF ACETIC ACID

It has already been mentioned that Bonner and Arreguin first indicated the undeniable role of acetic acid in the biosynthesis of *cis*-polyisoprene. Later, the studies of Chrastil and of Vyvalko substantiated the work of Bonner and Arreguin without adding new evidence to the theory.

Overlooking the chronological sequence, it should be mentioned, that Gascoigne and coworkers²³ detected coenzyme A in the latex of hevea and in the Kok-saghyz (this coenzyme is necessary to the metabolism of acetic acid).

The authors isolated from beef liver an enzyme activating the reaction:



The amount of sorbyl coenzyme A formed can be measured by spectrophotometry at wavelength 295 $m\mu$ ¹²⁶. Added to either centrifuged and freeze-dried serum (55.000 g, Moir¹²⁷) or to the freshly dialyzed product of latex, this enzyme transforms the additional sorbic acid to sorbyl coenzyme A. Therefore, it is possible to evaluate the coenzyme A content of latex. The results obtained are listed in Table Va.

TABLE VA

	Medium	Coenzyme A content: moles per 100 mg of dry substance
Hevea	Freeze-dried serum	
	- 2.5 years after preparation	0.02
	- 7 months	0.10
	- 2 months	0.16
	Dialyzation product of fresh latex	0.66
Kok-saghyz	Roots	0.27

Fresh latex, and with still more reason the laticiferous cells of hevea contain coenzyme A. Since the CH_3COO^- ion is transformed into rubber, the cell must also contain the enzyme which makes possible the following condensation:



By adding hydroxylamine (hydroxamate formation gives purple coloration with ferric chloride) Patrick¹²⁸ and later Kekwick¹²⁹ attempted to demonstrate acetic acid formation within the latex by decomposing acetyl Co A as it was formed. Unfortunately, hydroxylamine also blocks enzymic reactions. Furthermore, these authors used latex originating from a 4 year old tree, cultivated in a green house and the latex therefore was very different from normal latexes. Our own studies made in Viet Nam show the yield of sodium acetate ^{14}C transformation to vary largely between an untapped tree and a frequently tapped tree:

	Yield, %
Normally tapped tree	10 to 30
Untapped tree	0.25 to 1

For the purpose of testing rubber formation, a normal latex must originate from a regularly tapped tree.

TABLE Vb

Treatment	14 days*		28 days*	
	Rubber, mg/g bark	Increase, %	Rubber, mg/g bark	Increase, %
Control	12.4	9.4	—	—
Sodium acetate	18.4	48	13.9	48
Sodium methylcrotonate	16.0	29	8.8	6
Sucrose	13.8	11	9.5	0
Vitamins and oligoelements	14.0	13	9.5	0
Isoprene	14.4	16	9.2	-2

* Amounts of rubber contained in the bark. Samples taken 14 and 28 days after start of experiment.

In his studies on the physiology of hevea, Teas¹⁹ contributes useful details on the transformation of tagged sodium acetate to *cis*-polyisoprene. In the first part of his work, Teas studied the influence of untagged sodium acetate upon the production of hevea by evaluating the rubber content of small bark sections into which the chosen promoter was injected. The results obtained by Teas are listed in Table Vb. They should be studied in respect to those described by Baptiste¹³⁰, who has shown the influence of sodium acetate injections upon the production of hevea.

In the second part of his work, Teas used marked precursors. While repeating his earlier experiments, Teas also studied better ways of introducing the promoter into the area where the synthesis of rubber takes place, as will be described below.

1. Incorporation into bark segments

The injection of labelled sodium acetate into bark segments does not yield radioactive rubber. The labelled sodium acetate does not seem to penetrate the bark and such results contradict the earlier experiments of Teas and those of Baptiste¹³⁰.

2. Incorporation into embryo cultures

At a certain development stage of hevea seed, Teas transplanted a cotyledon into a flask, containing white medium (2% sucrose in agar-agar). The flasks with the experimental embryos also contained radioactive sodium acetate with a specific activity of 8.000 cpm/mg. Teas obtained the results indicated in Table Vc.

Despite the low specific activity of the recovered polyisoprene, the results indicate that the acetate was transformed into rubber.

TABLE Vc

INCORPORATION OF MARKED SODIUM ACETATE INTO EMBRYO CULTURES

Addition	Duration of the experiment, days	Weight of sample	Radioactivity of the rubber, cpm/mg
Control	—	170	—
Sodium acetate	18	213	59
Control	—	167	—
Sodium acetate	14	164	51

3. Incorporation of labelled sodium acetate into seedlings

Teas repeated the experiments of Bonner and Arreguin with hevea seedlings instead of guayule plants and indicated that the rubber extracted from the plants was radioactive, but that the scatter of results did not allow the conclusion that acetate was the only source for the isoprene unit.

TABLE VD
INCORPORATION OF RADIOACTIVE SODIUM ACETATE INTO *cis*-POLYISOPRENE
TISSUE CUTTINGS

Substrate	Radioactivity of substrate in cpm/micromoles	Weight of tissues after extraction with acetone	Total number of counts in the rubber	Substrate incorporated (micromoles)	Yield (based on acetate $2^{14}\text{C} = 1$)
Acetate 2^{14}C	6.92×10^3	35	3,782	0.0055	1.00
Pyruvate 2^{14}C	6.14×10^3	31	612	0.0010	0.18
Acetate 1^{14}C	1.93×10^3	138	387	0.0020	0.67
Acetate 2^{14}C	2.45×10^3	143	738	0.0030	1.00
Methyl crotonate 1^{14}C	0.270×10^3	140	30	0.0011	0.37
Methyl crotonate 3^{14}C	0.654×10^3	139	18	0.0003	0.10
Acetate $1,2^{14}\text{C}$	4.82×10^3	374	4,357	0.0090	1.00
Pyruvate 2^{14}C	6.14×10^3	378	1,063	0.0017	0.19
Sucrose uniformly marked	1.12×10^3	382	64	0.0006	0.07

4. Incorporation of labelled sodium acetate into tissue segments

By incubating for 16 hours some stem cuttings from seedlings in an adequate medium containing various tagged promoters, Teas obtained the results given in Table Vd. On these results, he bases a remark of prime importance: the yields of transformation of acetate into polyisoprene depend on the position of the marked carbon. The acetate- 1^{14}C ($\text{CH}_3\text{--}^{14}\text{COO}^-$) has an efficiency equal to $\frac{2}{3}$ of that of acetate- 2^{14}C ($^{14}\text{CH}_2\text{--COO}^-$). According to Teas, of the five carbon atoms of the isoprenic unit, three originate from the methyl group and only two from the carboxyl group of acetic acid. He compared an important part of the biosynthesis of polyisoprene with the theory proposed by Rudney⁸² concerning the marked β -hydroxy β -methylglutaric acid (cf. page 1263).

5. Preparation of tissue extracts

Preparations made by pulverizing frozen tissues and extracting the water soluble fraction have given no significant results.

6. Incorporation into the latex

Teas, in collaboration with Bandurski, used fresh latex as enzymatic medium and conducted his experiments by adding the substances listed in Table Ve.

TABLE VE

Latex	0.1 ml
Mixture of cofactors	0.1 ml
ATP, Co A, DPN, magnesium, fructose diphosphate, potassium phosphate EDTA	
Sodium acetate $5 \cdot 10^6$ cpm + distilled water + sucrose pH 7.0, incubation at 37°C	0.1 ml

The study of the influence of incubation time and volume of the medium confirms that the transformation of acetate to polyisoprene is entirely an enzymatic reaction.

Teas extended his experimentation to other precursors and indicated that the latex could transform in vitro certain promoters into polyisoprene as indicated in Table Vf.

TABLE Vf

Substrate	Radioactivity of rubber in cpm/mg	Counts incorporated per 10 ⁴ counts administered
Sucrose	0	0
Carbon dioxide	0	0
Methyl crotonate	11	16
Pyruvate	42	25
Acetate	207	41

Teas also noted, that levulinic acid obtained by ozonolysis of a tagged rubber sample within experimental error presented the same specific radioactivity as the initial sample. This proves that the acetate used as precursor certainly is incorporated into polyisoprene.

Teas studied the aptitude of other plant species to transform marked sodium acetate into rubber. He used thin slices as enzymatic media (Table Vg). He extended his attempts to gutta-percha. Radioactivity was detected during all experiments, in *cis* as well as in *trans* configurations.

TABLE Vg

TRANSFORMATION OF MARKED ACETATE INTO POLYISOPRENE,
cis OR *trans*, BY VARIOUS PLANT SPECIES

Families	Species	Tissue studied	Rubber %	Incorporated radioactivity cpm/mg
Apocynaceae	Funtumia elast.	leaf	4.9	109
	Lanugia latifolia	leaf and stem	1.8	69
	Plumeria acutifolia	leaf	3.8	74
	Plumeria rubia	leaf	2.2	20
	Tabernaemontana panducqui	stem	1.8	54
	Thevetia nereifolia	stem	0.5	22
Asclepiadaceae	Calotropis procera	stem	2.7	27
	Cryptostegia madagascariensis	stem	0.5	27
	Periploca sp.	leaf	0.6	35
Euphorbiaceae	Euphorbia tirucalli	stem	2.0	96
	Hevea brasiliensis	stem	4.5	70
	Manihot glaziovii	leaf	2.7	20
	Euphorbia pulcherrima	leaf and stem	0.9	35
Moraceae	Castilla elast.	leaf	0.8	46
	Ficus benjamina	stem	1.0	28
	Ficus elast.	leaf	1.3	19
	Ficus nota	leaf	0.5	24
Gustiferae	Clusia rosea	leaf	0.7	10
	Mimusops caffra	stem	1.9	40

gutta-percha
%

The yields of transformation indicated by Teas were very low, but it should be mentioned, that he diluted the latex used and it was later found that such dilution produced changes, which can prevent altogether the genesis in vitro of rubber. Also, he did not mention whether the trees he used were tapped regularly or not, which is a fact of prime importance (cf. remark page 1288).

This could probably explain, why Gascoigne and Jones¹³¹ and later Park¹³² could not reproduce the experiments of Teas and Bandurski with diluted fresh latex.

During our experiments carried out in Viet Nam, we noticed that the dilution of 1 cc of latex with an equal volume of water caused a complete stop in the transformation of sodium acetate 2^{14}C to rubber.

INCUBATION OF $5\text{ }\mu\text{C}$ OF SODIUM ACETATE 2^{14}C IN 1 CC OF LATEX
DURING 3 HOURS AT 28°C

Medium	Radioactivity of rubber in cpm/mg	Yield in %
Diluted latex	0	0
Nondiluted latex	8.000	31

Summarizing, we find in Teas' work three new facts:

(1) For the construction of an isoprenic unit, the biosynthesis of rubber utilizes three carbon atoms from the methyl group and two from the carboxyl group of acetic acid. Acetic acid serves as substrate in numerous plant species which produce rubber.

(2) The latex is an enzymatic medium able to ensure the transformation of sodium acetate to *cis*-polyisoprene.

(3) The radioactivity of rubber is recovered in levulinic acid produced by ozonolysis, which removes the possibility of a contamination of rubber.

Park and Bonner³¹ have nourished Kok-saghyz plants (*Taraxacum Kok-saghyz*) with sodium acetate marked on C1 or C2. After degradation of levulinic acid obtained by ozonolysis of rubber samples (Figure 5a), they could prove that the methyl group of levulinic acid was not radioactive (Table Vh) if acetate 1^{14}C served as substrate. This according to them, would confirm the sequence:

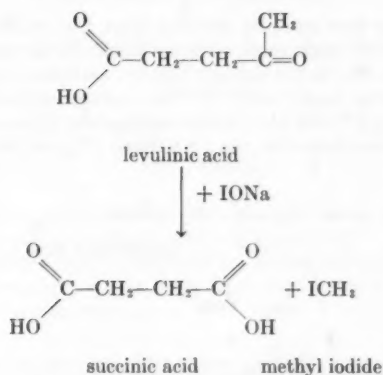


In fact, this statement does not contradict the now classical reaction:



TABLE VH
RESULTS OF PARK AND BONNER: INCORPORATION OF MARKED
ACETATE INTO KOK-SAGHYZ

	Radioactivity in cpm/ 10^{-4} moles of rubber	
	Sodium acetate 1^{14}C 3.5 me/m moles	Sodium acetate 2^{14}C 1 me/m moles
Crude rubber	970	5.340
Levulinic acid (2,4-di-nitrophenylhydrazone)	758	3.190
Methyl group (iodoform)	2	1.000
Rest of the molecule (succinate)	785	—

FIG. 5a.—Degradation of levulinic acid according to Park and Bonner⁹.

Later, Teas¹³ confirmed his earlier results by determining the position of marked carbons in levulinic acid, depending on whether ^{14}C or ^{214}C sodium acetate had been used.

A polyisoprenic chain with numbered carbons is considered in Figure 5b:

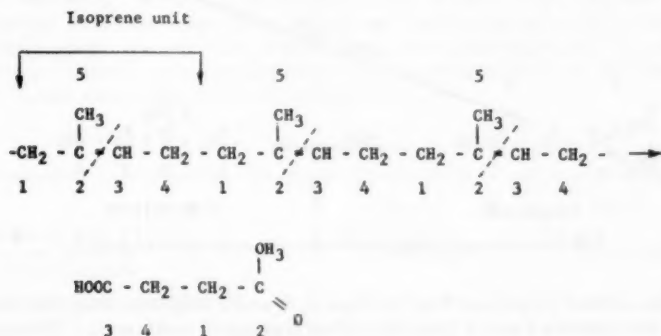


FIG. 5b.—Ozonolysis of polyisoprene to form levulinic acid. Slanted dashed lines indicate cleavage points.

Two rubber samples, obtained by incubation of sodium acetate marked in positions 1 and 2 respectively produced levulinic acid by ozonolysis. Further

TABLE VI
RADIOACTIVITY OF CARBONS IN AN ISOPRENE UNIT, ACCORDING TO TEAS

Radioactivity of carbons, cpm Carbon No.	Origin of activity	
	Sodium acetate ^{14}C	Sodium acetate ^{214}C
1	3	68
2	270	11
3	6	70
4	230	3
5	4	87

degradation of the two samples showed that the radioactive carbons were located differently in each case. From Table Vi it can be deduced, that carbons 2 and 4 are due to the carboxyl group, carbons 1, 3 and 5 to the methyl group of the original acetic acid. If the carbon originating from a methyl group is designated C* and the carbon originating from a carboxyl group C⁰, the following reaction sequence can be written (Figure 5c):

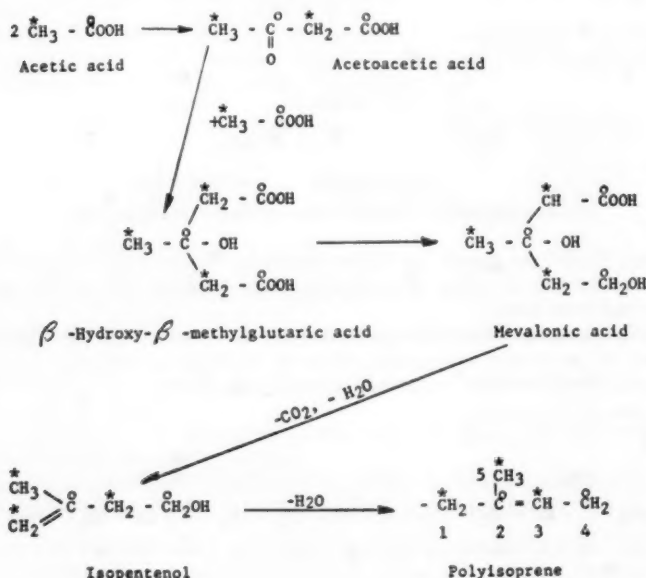


FIG. 5c.—Marking of polyisoprene formed from acetic acid $^{14}\text{C}^0$ or $^{24}\text{C}^*$.

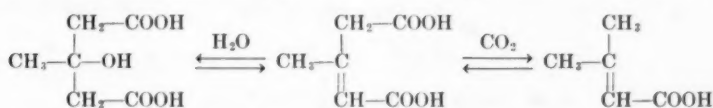
This scheme points out that carbons 1, 3 and 5 originate from the methyl group and carbons 2 and 4 from the carboxyl group of acetic acid. The experimental evidence given by Teas shows the extent of its validity. Thus, this work confirms the preeminent role of acetic acid in the biosynthesis as well as the fact that the mechanism follows the common rule of all terpene synthesis.

It is surprising that such low radioactivity should allow one to solve so complex a problem. That the sensitivity of isotopic methods justifies such interpretations and differences as the ones found in Table Vi is significant in all points.

B. EVIDENCE FOR THE FUNCTION OF β -METHYLCROTONIC ACID

Most authors quoted so far indicate that β -methylcrotonic acid is metabolized, whether it is introduced in various plants, through the roots (Bonner and Arreguin^{28, 29}), the leaves (Vyvalko and coworkers^{52, 53, 54}), or into fresh latex (Teas¹⁹). But β -methylcrotonic acid is not metabolized as efficiently as acetic acid. It had been indicated by Johnston¹³⁴ that β -methylcrotonic acid could

originate from a dehydration reaction of β -hydroxy- β -methylglutaric acid:



The reverse reaction is possible and β -hydroxy- β -methylglutaric acid can be synthesized from β -methylcrotonic acid (cf. page 1292).

Thus β -methylcrotonic acid considered by earlier theories to be an intermediate in the reaction chain which leads from acetic acid to polyisoprene, in reality, is only part of a side reaction.

C. EVIDENCE FOR THE FUNCTION OF MEVALONIC ACID

So far, mevalonic acid has not been characterized in rubber plants. Nevertheless, various studies demonstrate the transformation of this precursor of terpenes into polyisoprene.

Park and Bonner²¹ were first to indicate that mevalonic acid could be transformed into *cis*-polyisoprene in an enzymatic medium made of fresh latex.

They used latex originating from seedlings cultivated in greenhouses and in height measuring 1 meter and producing a latex, therefore, very different from the normal kind (cf. page 1288). Park and Bonner as estimated necessary cautiously added the cofactors in solid form, thus avoiding coagulation of the sample by dilution. The composition of the reaction mixtures is indicated in Table Vj and the results obtained in Table Vk.

TABLE Vj
COMPOSITION OF REACTION MIXTURES ACCORDING TO PARK AND BONNER

	Exp. 1	Exp. 2
Mevalonic acid 2 ¹⁴ C	10 moles	5 moles
0.1 mc/m moles	(5.4 · 10 ⁵ cpm)	(2.4 · 10 ⁶ cpm)
0.9 mc/m moles		
Diphosphopyridine nucleotide		0.01 mg
Coenzyme A		0.01 mg
Adenosine triphosphate		0.01 ml 0.1 M
Magnesium fructose diphosphate		0.02 ml 0.1 M
Latex	0.5 ml	0.4 ml

TABLE Vk
RESULTS OF PARK AND BONNER'S EXPERIMENTS; SUBSTRATE MEVALONIC ACID 2¹⁴C, FRESH LATEX MEDIUM

	Sp. act. (cpm/10 ⁻⁵ molecules of rubber, i.e. cpm/10 ⁻⁴ · 68 g)	
	Exp. 1	Exp. 2
Crude rubber	295	515
Levulinic acid	75	326
Iodoform	0	0
Succinate		307
—COOH		30
—CH ₂ (by difference)		277

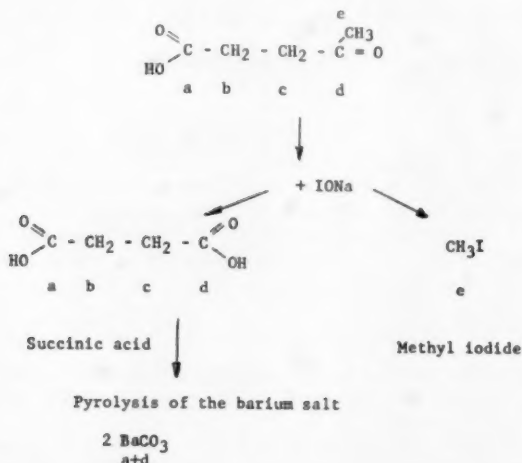


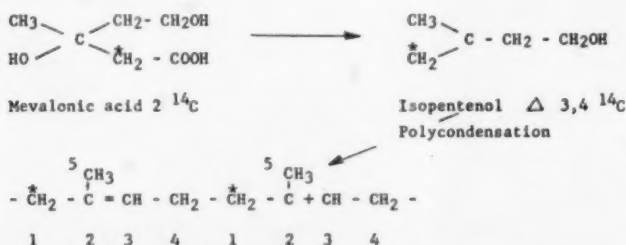
FIG. 5d.—Degradation of levulinic acid according to Park and Bonner.

The studies by Park and Bonner are of great interest. They successfully located the position of the marked carbon in the isoprene unit through study of the degradation products of levulinic acid, itself a product of marked rubber ozonolysis. The degradation of levulinic acid follows the sequence in Figure 5d.

According to Table Vk, neither carbon e nor carbons a and d are marked, therefore the radioactivity of levulinic acid is due to carbons b or c.

Carbons b and c of levulinic acid correspond to carbons 4 and 1 of successive isoprene units (Figure 5b).

Because the mevalonic acid used is marked on carbon 2, the following sequence must occur (Figure 5e):

FIG. 5e.—Theoretical marking of *cis*-polyisoprene obtained from mevalonic acid 2¹⁴C.

It follows, that carbon 1 is marked, a fact verified by the experimental results indicated before.

In a second step, Park and Bonner attempted to prove that radioactive levulinic acid originated from high molecular weight molecules and not from degradation of short chain molecules such as squalene.

Short chain molecules such as farnesol and squalene can produce levulinic

acid, but also liberate acetone corresponding to the ozonolysis of their terminal group (Figure 5f):

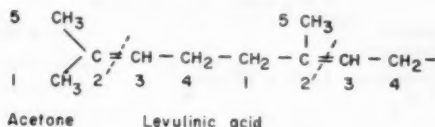


FIG. 5f.—Formation of acetone by ozonolysis of terminal groups.

In order to reject the degradation of short chain molecules, the authors trapped the volatile fractions of the ozonolysis reaction in a solution of 2, 4-dinitrophenylhydrazine.

According to Figure 5e, the use of mevalonic acid 2^{14}C should result in a molecule containing radioactive carbon in position 1. No radioactivity was detected in the trap, even when nonradioactive acetone was used as a carrier. Thus, the relative amount of terminal groups is very small compared with the number of isoprene units. For squalene, the proportion would be 1 to 6. Therefore, the molecules generating levulinic acid are of very high molecular weight. Lynen³² later confirmed this finding.

As an approximation, it is possible to calculate the molecular weight of the rubber sample exposed to ozonolysis by Park and Bonner, by basing the calculations on the relative error in the measurement of radioactivity in the trap of ± 2.5 cpm. This error represents a maximum margin of 5 cpm which could be due to radioactive acetone. Considering Table Vk, this amounts to possibly 1.4 chain ends per 98.6 isoprene units. The molecular weight of such a chain would therefore be at least:

$$\frac{98.6 \cdot 68}{1.4} = 4750$$

Even with these assumptions, the average molecular weight of the polyisoprene chains undergoing ozonolysis (after purification) is at least 4750. Under these circumstances, the presence of levulinic acid can no longer be ascribed to the ozonolysis of impurities.

The results of Park and Bonner confirm the role played by mevalonic acid in the biosynthesis of rubber. Although their demonstration is rigorous, their conclusions are weakened by the low yield in the transformation of mevalonic acid to polyisoprene. This yield is about 2%, compared with 45% yield found for the transformation of mevalonic acid to cholesterol in rat liver homogenates. Yields of 2, 45 or 9% correspond in reality to yields of 4, 90 and 18%, because only the active form of the racemic mixture of mevalonic acid is metabolized.

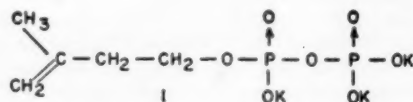
The NRPR group¹³⁵ eliminated any doubt by demonstrating that mevalonic acid could be incorporated into polyisoprene with 9% yield. The British researchers used fresh latex from a hevea cultivated in a greenhouse in Birmingham. In this latex, mevalonic acid was incubated for 3 hours at 28° C and the rubber purified by an original method, whereby short molecules as well as β -carotene were eliminated by dialysis. The radioactivity of the rubber produced together with the radioactivity of the resulting levulinic acid showed the yield mentioned above and led to the conclusion that mevalonic acid was in fact transformed into a high molecular weight product.

TABLE VI

Sodium mevalonate ^{24}C	0.33 μ moles	
	0.33 μ moles 2.5×10^5 cpm	
Potassium salt of isopentenyl pyrophosphate ^{14}C		0.9 μ moles 1.6×10^5 cpm
Radioactivity of 2,4-dinitrophenylhydrazone of levulinic acid	1.525×10^4 cpm	
Yield	0.0206 μ moles = 6.15%	0.234 μ moles = 26%

D. EVIDENCE FOR THE FUNCTION OF ISOPENTENYL PYROPHOSPHATE

In a masterful paper, Lynen and Henning²² demonstrated the role of isopentenyl pyrophosphate in the biosynthesis of *cis*-polyisoprene. They first verified that fresh latex originating from *hevea brasiliensis* cultivated in a greenhouse at Ludwigshafen converted the potassium salt of isopentenyl pyrophosphate ^{14}C into radioactive rubber in much better yields than the potassium mevalonate ^{24}C (Table VI). The formula of the potassium salt of isopentenyl pyrophosphate is:



They next demonstrated that the potassium salt of isopentenyl phosphate ^{14}C was not metabolized (Table Vm).

These two experiments clearly indicate the place of isopentenyl pyrophosphate within the reaction sequence which leads to *cis*-polyisoprene. In order to prove that the radioactivity of the rubber was not due to small molecules such as squalene (C_{30}), lycopene (C_{40}) or solanesol (C_{45}), the authors repeated the same experiments with isopentenyl pyrophosphate ^{44}C . The radioactivity of the acetone produced during ozonolysis by the terminal groups was evaluated similarly to the procedure of Park and Bonner (see Figure 5g) (Table Vn).

The absence of radioactivity in the acetone fraction proves that levulinic acid results from the ozonolysis of high molecular weight material. To reinforce this conclusion, a rubber sample was submitted to ultracentrifugation. By starting out with 0.7 ml cyclohexane with 0.25% rubber (total activity = $2.4 \cdot 10^4$ cpm), they obtained after 8 hours of centrifugation at 187,000 g three

TABLE Vm

Potassium salt isopentenyl phosphate ^{14}C	0.433 μ moles 1.6×10^5 cpm	0.433 μ moles 1.6×10^5 cpm
Potassium salt of isopentenyl pyrophosphate ^{14}C	—	0.9 μ moles 1.6×10^5 cpm
Radioactivity of 2,4-dinitrophenylhydrazone of levulinic acid	0	2.96×10^4 cpm
Yield	0	0.166 μ moles = 18.5%

Latex: 150 mg, incubation 4 hours at 26°C .

TABLE V^N*

Potassium salt of isopentenyl pyrophosphate ¹⁴ C		0.9 μ moles $1.6 \cdot 10^5$ cpm
Potassium salt of isopentenyl Pyrophosphate ⁴ C	0.227 μ moles $1.7 \cdot 10^5$ cpm	
Radioactivity of 2,4-dinitrophenyl-hydrazone of levulinic acid	$1.36 \cdot 10^4$ cpm	$1.3 \cdot 10^4$ cpm
Radioactivity of 2,4-dinitrophenyl-hydrazone of acetone	0	0
Yield	0.018 μ moles = 8%	0.073 μ moles = 8.15%

fractions of increasing molecular weight. The first fraction was only slightly radioactive, but the two others showed radioactivity of 5,000 and 15,000 counts, respectively. Thus, the high molecular weight fractions were most radioactive. Lynen tentatively suggested a molecular weight of $1 \cdot 10^6$ for the last fraction.

Almost simultaneously, the NRPR¹³⁶ confirmed the importance of isopentenyl pyrophosphate in obtaining 97% yield in the transformation of this substrate to *cis*-polyisoprene. The quality of the latex collected from *hevea brasiliensis* grown in a greenhouse could explain this result (cf. remark page 1288).

E. CONCLUSIONS

Altogether, this fragmentary information shows, that the biosynthesis of *cis*-polyisoprene is but a special case of the biosynthesis of terpenes, since the main steps are the same. This conclusion justifies the sequence proposed at the beginning of this text (cf. page 1232, Figure 1a). Despite the satisfaction of having characterized the mechanism of rubber formation (see, however, McMullen¹⁴) much has yet to be done in the field of physiology. The question of how to use the information to improve the production of the plant is still unanswered. The complexity of the enzymatic reactions described in section IV hinder a reasonable approach to the problem without becoming lost in too much theoretical research objectives. Should the study include the photosynthesis, the formation of reserves in the plant or should it be limited to a study of transformations taking place within the laticiferous cell? Even then, does the yield of the tree depend on the glycolysis, the Krebs cycle, or the transformation of acetate to rubber?

Fortunately, some information exists outside of the field of biosynthesis which brings valuable suggestions on how to circumscribe the problem.

VI. PHYSIOLOGY OF HEVEA BRASILIENSIS AND BIOSYNTHESIS OF *cis*-POLYISOPRENE

A great number of facts of often little known significance should be taken into account in this section. The danger of speculation without solid experimental basis should be recognized.

A list of known facts will help us to state the problem which concerns us. How can our knowledge of the mechanism of rubber synthesis help us to increase the yield of *hevea*?

Such an investigation made in detail would be impossible. It would imply the study, from photosynthesis to rubber formation, of thousands of enzymatic reactions concerning each tissue without the certitude of including the steps

* Starting latex, 180 mg. incubation 4 hours at 26° C.

which effectively determine the production. In fact, these reactions are interdependent and their individual response would be different in a living complex.

The scope of the problem has therefore to be limited, without eliminating some mechanisms on the basis of criteria limited to very particular circumstances.

Since the reason for the presence of rubber in the plant is unknown, this first objective will have to be reached without considering its physiological role. Because of the very low rubber content of certain plants, rubber cannot be considered to be a reserve, defense or waste product.

The hevea tree responds to regular tapping by producing more and more latex, up to a certain limit. Thus, hevea which is one of the few species enjoying this property, must have an adequate supply of carbon to produce the effect induced by the tapping. It is known, that photosynthesis is the mechanism contributing by far the most carbon to the plant development by transforming carbon dioxide from the air into glucides (see Figure 2f).

Unfortunately, these facts become less evident, when the photosynthesis of the tree is correlated with its production. Nevertheless, the following points can be considered:

(1) There is not always a difference between the leaves of an efficient and a mediocre tree grown in the same lot, both being from the same clone.

(2) Scully¹²⁷ exposed young hevea plants to an atmosphere of carbon dioxide marked with ^{14}C . The rubber became rapidly radioactive, proving that the products of photosynthesis readily reach the laticiferous cells.

(3) Chilov⁵⁶ described a contradictory experiment made under similar conditions with Kok-saghyz plants. The plants were placed in an atmosphere of carbon dioxide ^{14}C and the radioactivity of their carotene and rubber content determined in function of time. The radioactivity of the carotene increased rapidly after a few hours of exposure, then decreased and increased again after 80 hours. The radioactivity of rubber increased very slowly but regularly (Figure 6a).

The findings suggest that, contrary to the carotene producing cells, the laticiferous cells of Kok-saghyz are supplied with marked products after the

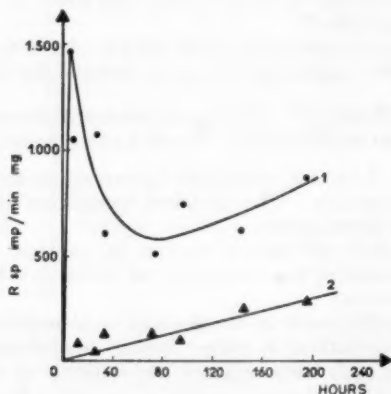


FIG. 6a.—Variation of the specific radioactivity of carotene (1) and of rubber (2).

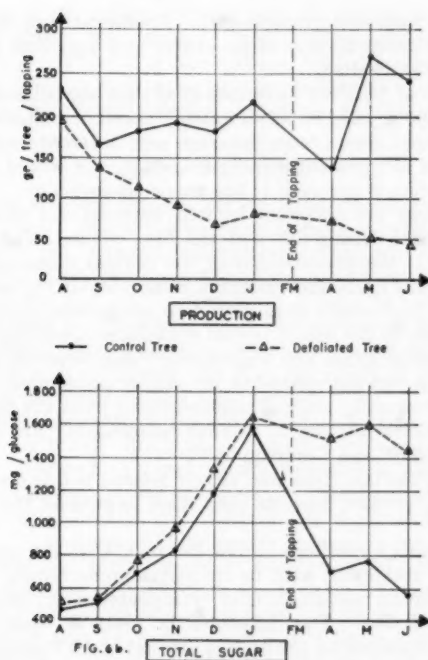


FIG. 6b.—Total sugar. Time in months.

action of photosynthesis, as if there would be reserves used only under necessity. This would also explain the increase in radioactive carotene after 80 hours.

(4) D'Auzac and Pujarniscle¹³⁸ have measured over a period of almost one year the production of a hevea tree without leaves. Figure 6b summarizes their findings. They conclude that: (1) Having lost most of its ability for photosynthesis, the tree continues to produce appreciable amounts of rubber. A small amount of cells containing chlorophyll are located in the bark, but the surface area of the bark is not comparable with that of the leaves. And (2) the amount of glucides increases in the latex.

These findings, and the fact that the reserves of the wood have decreased during this time, suggest that the catabolism of glucides, strongly connected to the rotation of phosphorous and magnesium, is one of the interesting points to be studied. Photosynthesis does not figure as a factor which limits the production of rubber.

Despite Scully's work, carried out on young hevea, it appears that photosynthesis is not coupled to the production of polyisoprene, or at least, that glucidic reserves act as buffers between the mechanism of production and that of utilization of these reserves.

On the other hand, d'Auzac and Pujarniscle¹³⁹ have shown that no relationship exists between the bark's content in hemicellulosic reserves and glucides and the production of rubber. Particularly, heavy rubber production does not change the amount of these reserves. This suggests, that the reserves of hevea

are abundant and frequently replenished. Photosynthesis does not regulate the production of hevea to any large extent and therefore is not the most urgent problem to be studied.

The researchers of NRPR have indicated that isopentenyl pyrophosphate is transformed in 100% yield to polyisoprene¹³⁶, even in a latex originating from a young and untapped tree, a latex therefore very different from normal latexes and almost unable to metabolize sodium acetate. It would not seem either that polycondensation is involved in the tree's productivity.

The crucial steps are therefore located between the penetration of the glucides into the laticiferous cell and the final phase. The list of possible factors includes: (1) the permeability of the cellular membrane, (2) the glycolysis, (3) the Krebs cycle and oxidative phosphorylation, and (4) the transformation leading from acetyl coenzyme A to isopentenyl pyrophosphate.

The permeability of the cell to carbon containing compounds does not seem to interfere, because d'Auzac and Pujarnicle¹³⁹ also observed that the glucide content of the latex was not related to the rubber production, as if the supply of glucides would normally proceed independently from the amount of rubber formed. The theories relative to cellular permeability are discussed in the papers by Schweitzer¹⁴⁰ and Compagnon¹⁴¹.

It appears that the last three and closely related points could be the object of most interesting studies, because they seem to contain the key to the productivity of hevea.

In support of this hypothesis comes the fact, that the maximum yield of transformation of mevalonic acid to *cis*-polyisoprene hardly exceeds 10%¹³⁵. But the transformation mevalonic acid \rightarrow isopentenyl pyrophosphate only requires ATP as cofactor. The difference in yield of those two precursors (cf. page 1297) is explained by the limited amount of ATP contained in the latex *in vitro*, thereby limiting the phosphorylation of MVA. In the living tree it is believed that the yield of this reaction is conditioned by the action of the cofactor and by the possibility of regenerating the latter (transformation of ADP to ATP). Ultimately, the formation of isopentenyl pyrophosphate depends therefore on the oxidative phosphorylation and on glycolysis.

Glycolysis, or transformation of one molecule of hexose to two molecules of acetyl coenzyme A, is coupled to the regeneration of two molecules of ATP from two molecules of ADP. Thus, three hexose molecules correspond to the formation of six molecules of acetyl coenzyme A which lead to two molecules of mevalonic acid and six molecules of ATP. The transformation of mevalonic acid to isopentenyl pyrophosphate requires six molecules of ATP. Glycolysis therefore produces enough ATP for the phosphorylation of mevalonic acid and for the decarboxylation (cf. page 1274). Nevertheless, the cell certainly consumes more than this amount of ATP in order to achieve the other transformations and it is hardly conceivable that oxidative phosphorylation should not intervene.

The roles of the phosphates was emphasized by d'Auzac and Pujarnicle¹⁴² who have demonstrated, that any increase in rubber production was coupled with an increase in the amount of inorganic and organic phosphorous present in the latex. This increase can be interpreted as an intensive rotation of organic substances:



This rotation of phosphorylated cofactors is closely dependent upon the Krebs cycle (cf. Figure 2h), which in turn is dependent upon the supply of acetyl coenzyme A. Thus, it is our opinion, that glycolysis which produces acetyl coenzyme A is the most important mechanism to be studied because its functioning seems to control directly and indirectly the productivity of the laticiferous cells.

VII. CONCLUSIONS

The goal seems now well defined, but the means necessary for its attainment have yet to be chosen. Undoubtedly, isotopic methods will be the appropriate approach to gather the required information. They will be used less for investigation of individual transformations than for establishing the balance of transformation of the precursors. Finally, it is very fortunate that latex can be broadly compared to a homogenate of laticiferous cells. Therefore, it is reasonable to believe that, used with precaution, the latex must reflect the ability of the tree to form rubber and that the study of the points that are mentioned will be possible by using this medium.

No matter how successfully the mechanisms limiting or controlling the rubber production will be located, it will remain a problem to modify them in the desired way, because the tree (*hevea brasiliensis*) forms a system in equilibrium. In this system, all reactions are interdependent and a reaction requiring manganese or calcium will interfere with those which are poisoned by these metals. . . . In short, it is impossible to modify entirely the plant life. Consequently, the action of the researcher will always be limited because drastic modifications of the state of equilibrium would cause undesirable effects. But just as medicine can modify certain metabolisms of a patient if it proceeds without brutality, it may be possible to act in a limited way upon the basic metabolisms of *hevea*. This does not mean that the productivity of the tree will not be changed considerably, but in any case the methods employed will have to be very mild.

Before reaching this goal, many important problems will have to be solved. As in medicine, identification of the basic metabolism will not suggest the therapeutic method for their acceleration. Without this background information, no treatment can be conceived, but no miracle drug results from diagnosis alone. The dual aspect of any studies in this field is striking: the immense possibilities anticipated are tempered by the problems involved in plant life.

In view of the scientific progress of the last five years, such a restrictive statement seems to be out of order. The evolution of our knowledge is so fast, that such preconceived ideas may rapidly become obsolete and so obscure our view for new progress.

We believe it necessary to conclude this review with such a warning, making the reader aware of the hopes as well as the limitations of the studies on the biosynthesis of *cis*-polyisoprene.

VIII. REFERENCES

- ¹ Bonner, J., and Galston, A., *Botan. Rev.* **13**, 543 (1947).
- ² Stewart, W. D., Wachtel, W. L., Shipman, J. J., Yanko, J. A., *Science* **122**, 1271 (1955).
- ³ Bouychou, J. G., "Manual of Planting Hevea," French Rubber Institute, Paris (1954).
- ⁴ Dijkman, H. J., "Hevea," Univ. of Miami Press, Coral Gables Florida, 1951, Chap. IX, p. 84.
- ⁵ Dixon, M., and Webb, E. C., "Enzymes," Acad. Press, Inc., N. Y. (1958).
- ⁶ Fruton, J. S., and Simmonds, S., "General Biochemistry," J. Wiley and Sons, Inc., N. Y., 1958, p. 381.
- ⁷ Andrews, E. H., and Dickenson, P. B., Proceedings of the Natural Rubber Research Conference (Kuala Lumpur 1960), p. 756 (Rubber Research Institute of Malaya).
- ⁸ Andrews, E. H., and Dickenson, P. B., Private communication.
- ⁹ Frey-Wyssling, A., *Arch. Rubber Cult.* **13**, 392 (1929).

- ¹⁰ Homans, L. N. S., and Van Gils, G. E., *Ind. Rubber J.* 114, 854 (1948).
- ¹¹ Verhaar, G., *Ind. Rubber World* 126, 636 (1952).
- ¹² Schmidt, E., *Bot. Zeitschrift* 40, 435 (1882).
- ¹³ Popovici, H., *Compt. rend.* 183, 143 (1926).
- ¹⁴ Bobilof, W., *Arch. Rubber Cult.* 9, 313 (1925).
- ¹⁵ Schweitzer, J., *Arch. Rubber Cult.* 26, 345 (1949).
- ¹⁶ Ruinen, J., and de Haan-Homans, L. N. S., *Arch. Rubber Cult.* 27, 243 (1950).
- ¹⁷ Sohoon, T. G. F., and Phos, K. L., *Arch. Rubber Cult.* 33, 195 (1956).
- ¹⁸ Wiersum, L. K., *Vakblad voor Biologen*, 37, 17 (1957); *R.G.C.* 35, 276 (1958).
- ¹⁹ Teas, H. J., and Bandurski, R. S., *J. Am. Chem. Soc.* 78, 3549 (1956); Teas, H. J., Polhamus, L., and Monterosso, J. C., *Abst. of Conf. on Radioactive Isotopes in Agriculture*, East Lansing, Michigan (January 1956), p. 15; Teas, H. J., and Bandurski, R. S., *Chem. Eng. News* 35, 74 (1957); Bandurski, R. S., and Teas, H. J., *Plant Physiol.* 32, 643 (1957).
- ²⁰ Archer, B. L., and McSweeney, G. P., (NRPR) Private communication.
- ²¹ Milanes, F. R., *Archives do Serviço Florestal* 2, 39 (1946).
- ²² Southorn, W. A., "Microscopy of Hevea Latex," Conf. on Natural Rubber, Kuala Lumpur (1960).
- ²³ Gascoigne, J. A., Overend, W. G., Moir, G. E. J., and Hubner, G. H., *Nature* 181, 628 (1958).
- ²⁴ van der Tempel, M., *Arch. Rubber Cult.* 31, 209 (1954).
- ²⁵ Hsia, R. C., *Trans. Inst. Rubber Ind.* 34, 267 (1958).
- ²⁶ Fournier, P., D'Ausac, J., Pujarnacle, S., and Tuong-Chi-Cuong, *Compt. rend.* 252, 196 (1961); *Rev. gén. caoutchouc* 38, 403 (1961).
- ²⁷ McMullen, A. I., *Biochem. J.* 72, 545 (1959); *Biochem. Biophys. Acta*, 41, 341 (1960).
- ²⁸ Bonner, J., and Arreguin, B., *Arch. Biochem.* 21, 109 (1949).
- ²⁹ Arreguin, B., and Bonner, J., *Arch. Biochem.* 26, 178 (1958).
- ³⁰ Arreguin, B., Bonner, J., and Wood, B. J., *Arch. Biochem.* 31, 234 (1951).
- ³¹ Park, R. B., and Bonner, J., *J. Biol. Chem.* 233, 340 (1958).
- ³² Lynen, F., and Henning, V., *Angew. Chem.* 72, 820 (1960).
- ³³ Harries, C., "Untersuchungen über die natürlichen und künstlichen Kautschukarten," J. Springer, Berlin (1919).
- ³⁴ Stewart, A. W., and Graham, H., "Recent Advances in Organic Chemistry," vol. 1, 5th edition, Longmans Green and Co., London (1931), p. 292.
- ³⁵ Hall, J. A., *Chem. Rev.* 20, 305 (1937).
- ³⁶ Nerdel, F., *Forschungen über Fortsch.* 26, Sonderheft 2, 19 (1950).
- ³⁷ Aschan, O., "Naphthalene Compounds, Terpenes and Camphor," Svenska Tekn. Vetenskapsakademien, Helsingfors, Finland, 1926.
- ³⁸ Ambros, O., *Rev. gén. caoutchouc* 133, 3 (1937).
- ³⁹ Prokofiev, A. A., *Bull. Acad. Science USSR*, (1939), p. 908.
- ⁴⁰ Robinson, R., *Congreso intern. Quim. pura y aplicada*, Madrid (1934); Summary C.A. 31, 1845 (1937).
- ⁴¹ Frey-Wyssling, A., Ernährung und Stoffwechsel der Pflanze und Iena, Tenafly, N. J., H. Felix Kraus (1946).
- ⁴² Zelinsky, N. D., and Rapoport, I. B., *Bull. Soc. Nat. Moscow* 49, 5 (1940).
- ⁴³ Hesse, G., Eilbracht, H., and Reicheneder, F., *Ann.* 546, 233 (1941).
- ⁴⁴ de Wildeman, E., *Bull. Classe Sc. Ac. Roy. Belg. 5e series*, 30, 169 (1944).
- ⁴⁵ Drobkov, A. A., *Bull. Acad. Science USSR* 53, 745 (1946).
- ⁴⁶ Polonovski, M., *Rev. gén. caoutchouc* 22, 133, 153 (1945).
- ⁴⁷ Calvin, M., Heidelberger, C., Reid, J. C., Tolbert, B. M., and Yankwich, P. E., "Isotopic Carbon," John Wiley & Sons, New York (1949), p. 180.
- ⁴⁸ Johnson, J. R., Record of Chemical Progress, Summer Issue, p. 137 (1950) by Friends of the Kresge-Hooker Scientific Library.
- ⁴⁹ Springborn, R. C., Thesis, Cornell University, 1955; *Dis. Abstr.* 15, 980 (1955).
- ⁵⁰ Chadha, M. S., Thesis, Cornell University, 1955; *Dis. Abstr.* 16, 449 (1956).
- ⁵¹ Chrastil, I., *Biologie Tchécoslovaque* 3, 382 (1954).
- ⁵² Vyvalko, I. G., and coll., *Ukrain. Khim. Zhur.* 22, 644 (1956).
- ⁵³ Vyvalko, I. G., and coll., *Ukrain. Khim. Zhur.* 22, 655 (1956).
- ⁵⁴ Vyvalko, I. G., and coll., *Ukrain. Khim. Zhur.* 23, 516 (1957).
- ⁵⁵ Chlilov, E. A., Louschevskaya, G., Matkovski, K., Savinov, B., Vyvalko, I., and Yasmikov, A., *Rev. gén. caoutchouc* 35, 1067 (1958).
- ⁵⁶ Teas, H. J., and Bonner, J., *Rev. gén. caoutchouc* 37, 1143 (1960).
- ⁵⁷ Barlow, G. B., and Patrick, A. D., *Nature* 182, 662 (1958).
- ⁵⁸ Ruzicka, L., and Stoll, M., *Helv. Chem. Acta* 5, 929 (1922).
- ⁵⁹ Reed, L. J., and Debuak, B. G., *J. Am. Chem. Soc.* 74, 2383 (1954).
- ⁶⁰ Mehler, A. H., "Introduction to Enzymology," Academic Press, N. Y., 1957, p. 73.
- ⁶¹ Gunzalus, I. G., and Smith, R. A., *Proc. Int. Symp. Enzyme Chem.*, Tokyo, Kyoto (1957), Acad. Press, N. Y. (1958), p. 77.
- ⁶² Reed, L. J., *Proc. Int. Symp. Enzyme Chem.*, Tokyo-Kyoto (1957); Acad. Press, N. Y. (1958), p. 71.
- ⁶³ Korke, M., and Reed, L. J., *J. Am. Chem. Soc.* 81, 505 (1959).
- ⁶⁴ Ugai, T., Tanaka, S., and Dokawa, S., *J. Pharm. Soc. Japan* 63, 296 (1943).
- ⁶⁵ Tamura, S., Tamura, R., and Arabe, H., *Proc. Japan Acad.* 27, 302 (1951).
- ⁶⁶ Breslow, R., *Chem. and Ind.*, p. 893 (1957).
- ⁶⁷ Ochoa, S., *J. Biol. Chem.* 138, 751 (1941).
- ⁶⁸ Littlefield, J. W., and Sanadi, D. R., *J. Biol. Chem.* 199, 65 (1952).
- ⁶⁹ Lynen, F., *Bull. soc. chim. biol.* 35, 1061 (1953).
- ⁷⁰ Knoop, F., *Beitr. Chem. physiol. path.* 6, 150 (1904).
- ⁷¹ Grunert, R. R., and Phillips, P. H., *Arch. Biochem.* 30, 217 (1951).
- ⁷² Flynn, R. M., Jones, M. E., and Lipmann, F., *J. Biol. Chem.* 211, 791 (1954).
- ⁷³ Ingraham, L. L., and Green, D. E., *Science* 128, 310 (1958).
- ⁷⁴ Crane, F. L., Mii, S., Hange, J. G., Green, D. E., and Beinert, H., *J. Biol. Chem.* 218, 701 (1956).
- ⁷⁵ Beinert, H., and Pace, E., *J. Biol. Chem.* 225, 465 (1957).
- ⁷⁶ Lynen, F., Wessely, L., Wieland, O., and Rueff, L., *Angew. Chem.* 64, 687 (1952).
- ⁷⁷ Lynen, F., and Ochoa, S., *Biochem. Biophys. Acta* 12, 299 (1953).
- ⁷⁸ Burton, K., and Ochoa, S., *J. Biol. Chem.* 199, 44 (1955).
- ⁷⁹ Lynen, F., *J. Cell. Comp. Physiol.* 54, suppl. 1, 33 (1960).
- ⁸⁰ Sjöberg, B., *Z. Physik. Chem.* B52, 209 (1942), Leipzig.
- ⁸¹ Pullmann, B., *Comp. rend. Ac.* 251, 1581 (1960); Pullmann, B., and Pullmann, A., *Proc. Nat. Acad. Sci.* 44, 1197 (1958).

- ⁸² Rudney, H., *J. Biol. Chem.* **227**, 363 (1957).
- ⁸³ Rudney, H., *J. Am. Chem. Soc.* **76**, 2595 (1954).
- ⁸⁴ Rudney, H., *J. Am. Chem. Soc.* **77**, 1698 (1955).
- ⁸⁵ Böcher, N. L. R., Overath, P., and Lynen, F., *Biochem. Biophys. Acta* **40**, 491 (1960).
- ⁸⁶ Chichester, C. O., Yokohama, H., Nakayama, T. O. M., Lukton, A., and McKinney, J. *Biol. Chem.* **234**, 598 (1959).
- ⁸⁷ Yokohama, H., Chichester, C. O., Nakayama, T. O. M., Lukton, A., and McKinney, J. *Am. Chem. Soc.* **79**, 2029 (1957).
- ⁸⁸ Amdur, B. H., Thesis, Harvard University, Cambridge, Mass. (1958).
- ⁸⁹ Bachhawat, B. K., and Coon, M. J., *J. Biol. Chem.* **231**, 625 (1958).
- ⁹⁰ Woessner, J. F., Bachhawat, B. K., and Coon, M. J., *J. Biol. Chem.* **233**, 520 (1958).
- ⁹¹ Lynen, F., Knappe, J., Lorch, E., Jötting, G., and Ringelman, E., *Angew. Chem.* **71**, 481 (1959).
- ⁹² Campillo, A. del, Campbell, A., Dekker, E. E., and Coon, M. J., *Biochem. Biophys. Acta* **31**, 290 (1959).
- ⁹³ Folkers, K., Shunk, C. H., Linn, B. O., Robinson, F. M., Wittreich, P. E., Huff, J. W., Gilfillan, J. L., Skeggs, H. R., "Ciba Foundation Symposium of Biosynthesis of Terpenes and Sterols," J. and A. Churchill, Ltd. London (1959); Shunk, C. H., Linn, B. O., Huff, J. W., Gilfillan, J. L., Skeggs, H. R., and Folkers, K., *J. Am. Chem. Soc.* **79**, 3294 (1957); Skeggs, H. R., Wright, L. D., Cresson, E. L., MacRae, G. D. E., Hoffman, C. H., Wolf, D. E., and Folkers, K., *J. Biol. Chem.* **232**, 519 (1956).
- ⁹⁴ Tamura, C., *J. Gen. Microbiol.* **2**, 431 (1956).
- ⁹⁵ Tavormina, P. A., Gibbs, M. H., and Huff, J. W., *J. Am. Chem. Soc.* **78**, 4498, 6210 (1956).
- ⁹⁶ Ferguson Jr., J. J., Durr, I. F., and Rudney, H., *Fed. Proc.* **17**, 219 (1958).
- ⁹⁷ Wright, L. D., and coworkers, *J. Am. Chem. Soc.* **79**, 6572 (1957).
- ⁹⁸ Wright, L. D., and Cleland, M., *Proc. Soc. Exptl. Biol. Med.* **96**, 219 (1957).
- ⁹⁹ Knappe, J., Ringelman, E., and Lynen, F., *Biochem. Z.* **332**, 195 (1959).
- ¹⁰⁰ Popjak, G., and Cornforth, J. W., *Adv. In Enzymology* **22**, 281 (1960).
- ¹⁰¹ Tabor, E., Mehler, A. H., and Stadtman, E. R., *J. Biol. Chem.* **204**, 127 (1955).
- ¹⁰² Durr, I. F., and Rudney, H., *J. Biol. Chem.* **235**, 2572 (1960).
- ¹⁰³ Lineweaver, H., and Burk, D., *J. Am. Chem. Soc.* **56**, 658 (1934).
- ¹⁰⁴ Wittling, L. A., and Porter, J. W., *J. Biol. Chem.* **234**, 2841 (1959).
- ¹⁰⁵ Rilling, H., Tohen, T. T., and Bloch, K., *Proc. Natl. Acad. Sci.* **44**, 167 (1958).
- ¹⁰⁶ Rilling, H., and Bloch, K., *J. Biol. Chem.* **234**, 1424 (1959).
- ¹⁰⁷ Tohen, T. T., *J. Am. Chem. Soc.* **79**, 6344 (1957).
- ¹⁰⁸ Lynen, B., "Ciba Foundation Symposium on the Biosynthesis of Terpenes and Sterols," J. A. Churchill, Ltd., London, 1959, p. 95.
- ¹⁰⁹ Henning, U., Kessel, I., and Lynen, F., "Abstr. Fourth Internat. Biochem. Congr.," Vienna, 1958, p. 47.
- ¹¹⁰ Popjak, G., Gosselin, L., Gore, I. Y., and de Waard, A., "Abstr. Fourth Internat. Biochem. Congr.," Vienna, 1958, p. 203.
- ¹¹¹ Levy, H. R., and Popjak, G., *Biochem. J.* **72**, 359 (1959).
- ¹¹² Levy, H. R., and Popjak, G., *Biochem. J.* **75**, 417 (1960).
- ¹¹³ Bloch, K., Chaykin, S., Phillips, A. H., and de Waard, A., *J. Biol. Chem.* **234**, 2595 (1959).
- ¹¹⁴ Henning, U., Möselein, E. M., and Lynen, F., *Arch. Biochem. Biophys.* **83**, 259 (1959).
- ¹¹⁵ Lynen, F., Eggerer, H., Henning, U., and Kessel, I., *Angew. Chem.* **70**, 738 (1958).
- ¹¹⁶ Yuan, C., and Bloch, K., *J. Biol. Chem.* **234**, 2605 (1959).
- ¹¹⁷ Eggerer, H., and Lynen, F., *Ann.* **630**, 57 (1960).
- ¹¹⁸ Agranoff, B. W., Eggerer, H., Henning, U., and Lynen, F., *J. Am. Chem. Soc.* **81**, 1254 (1959).
- ¹¹⁹ Agranoff, B. W., Eggerer, H., Henning, U., and Lynen, F., *J. Biol. Chem.* **235**, 326 (1960).
- ¹²⁰ Lynen, F., Agranoff, B. W., Eggerer, H., Henning, U., and Möselein, E. M., *Angew. Chem.* **71**, 657 (1959).
- ¹²¹ Popjak, G., *Tetrahedron Letters* No. 19, 19 (1959).
- ¹²² Popjak, G., Lowe, A. E., Moore, D., Brown, L., and Smith, F. A., *Lipid Research* **1**, 29 (1959).
- ¹²³ Wright, L. D., *Proc. Soc. Exptl. Biol. Med.* **96**, 364 (1957).
- ¹²⁴ Siperstein, M. D., and Fagan, V. M., *Science* **126**, 1012 (1958).
- ¹²⁵ Ogilvie, J. W., and Langdon, R. C., *J. Am. Chem. Soc.* **81**, 754 (1959).
- ¹²⁶ Hubscher, G., and Wakil, S. H., Unpublished work referred to in reference 23.
- ¹²⁷ Moir, G. F. J., *Nature* **184**, 1626 (1959).
- ¹²⁸ Patrick, A. D., *Nature* **180**, 37 (1957).
- ¹²⁹ Kekwick, R. G. O., private communication.
- ¹³⁰ Baptiste, E. D. C., *Ann. Report Rubber Res. Inst. Malays* (1949-1951), p. 90.
- ¹³¹ Gascoigne, J. A., and Jones, P., *Nature* **183**, 819 (1959).
- ¹³² Park, R. B., Ph.D. Thesis, California Institute of Technology, Pasadena, California (1958).
- ¹³³ Teas, H. J., and Rabinowitz, J. L., *Proceedings of the Natural Rubber Research Conference* (Kuala Lumpur 1960), p. 777 (Rubber Research Institute of Malaysia 1960).
- ¹³⁴ Johnston, J. A., Racusen, D. W., and Bonner, J., *Proc. Natl. Acad. Sci.* **40**, 1031 (1954).
- ¹³⁵ Kekwick, R. G. O., Archer, B. L., Barnard, D., Higgins, G. M. C., McSweeney, G. P., and Moore, C. G., *Nature* **184**, 268 (1959).
- ¹³⁶ Archer, B. L., Ayrey, G., Cockbain, E. G., and McSweeney, G. P., *Nature* **189**, 663 (1961).
- ¹³⁷ Scully, N. J., *Rubber Age* **73**, 86 (1953).
- ¹³⁸ d'Ausac, J., and Pujarniscle, S., *Proceedings of the Natural Rubber Research Conference* (Kuala Lumpur, 1960), p. 154 (Rubber Research Institute of Malaysia).
- ¹³⁹ d'Ausac, J., and Pujarniscle, S., *Rev. gén. caoutchouc* **36**, 1687 (1959).
- ¹⁴⁰ Schweitzer, J., *Arch. Rubber Cult.* **26**, 388 (1949).
- ¹⁴¹ Compagnon, P., and Tixier, P., *Arch. Rubber Cult.* (Special issue) May, 1953.
- ¹⁴² d'Ausac, J., and Pujarniscle, S., *Rev. gén. caoutchouc* **36**, 862 (1959).
- ¹⁴³ Kasiro, Y., Leone, E., and Ochoa, S., *Proc. Natl. Acad. Sci. (US)* **46**, 1319 (1960).
- ¹⁴⁴ McMullen, A. L., *Biochem. J.* **78**, 33P (1961).

KINETIC STUDIES OF THE VULCANIZATION OF NATURAL AND SYNTHETIC RUBBERS*

WALTER SCHEELE

KAUTSCHUKINSTITUT, TECHNISCHE HOCHSCHULE, HANNOVER, GERMANY

CONTENTS

	PAGE
I. Introduction.....	1307
II. Fundamentals of kinetics.....	1309
III. Kinetics of vulcanization processes.....	1312
A. Direct vulcanization by sulfur, the reaction of sulfur with natural and synthetic rubber.....	1313
1. Decrease of concentration of sulfur in the reaction of sulfur with natural rubber.....	1313
a. Temperature dependence of the rate.....	1315
b. Dependence of the rate on concentration.....	1317
2. Decrease of sulfur concentration in reaction with synthetic rubbers.....	1322
a. Temperature dependence of the rate.....	1322
b. Dependence of the rate on concentration.....	1322
3. The polysulfide bound sulfur in the reaction of sulfur with natural and synthetic rubbers.....	1325
4. Discussion of the experimental results.....	1328
B. Indirect, accelerated vulcanization of rubber by sulfur.....	1332
1. Time law of sulfur decrease and the temperature dependence of rate constants.....	1334
2. Dependence of the rate of sulfur decrease on concentration..	1339
3. Interpretation of the experimental results.....	1342
4. Nature of the intermediate compounds formed during ac- celerated vulcanization.....	1350
5. Some special cases of indirect vulcanization by sulfur.....	1354
a. Vulcanization in the presence of mercaptobenzothiazole (MBT) and zinc oxide or zinc diethyldithiocarbamate (ZnDEDC).....	1354
b. Vulcanization of natural rubber in the presence of MBT, zinc oxide, and Zn stearate.....	1357
c. Vulcanization of natural rubber in the presence of benzothi- azolyl disulfide (MBTS).....	1360
d. Vulcanization in the presence of sulfenamides.....	1364

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe.

C. Direct vulcanization.....	1367
1. Vulcanization of 1,5 polyenes by compounds of the thiuram series.....	1367
a. Direct thiuram vulcanization of natural and synthetic rubber.....	1367
b. Vulcanization of natural and synthetic rubber accelerated by thiuram compounds.....	1375
2. Vulcanization by peroxides.....	1380
D. The crosslinking reaction.....	1385
IV. Concluding considerations.....	1395
V. References.....	1400

The following abbreviations are used:

MBT	2-mercaptobenzothiazole
ZnMBT	zinc salt of MBT
CAMBT	cyclohexylamine salt of MBT
MBTS	2-benzothiazyl disulfide
TD	thiuram disulfide
TMTD	tetramethylthiuram disulfide
TMTM	tetramethylthiuram monosulfide
TETD	tetraethylthiuram disulfide (on figures, TÄTD)
ZnDC	zinc dialkyldithiocarbamate
ZnDMDC	zinc dimethyldithiocarbamate
ZnDEDC	zinc diethyldithiocarbamate
DPG	diphenylguanidine
CBS	N-cyclohexyl benzothiazyl sulfenamide
DIBS	N,N-diisobutyl benzothiazyl sulfenamide
SBR	styrene butadiene rubber (Buna S)
NBR	nitrile butadiene rubber (Perbunan)
NR	natural rubber (on figures, NK)

I. INTRODUCTION

The author thanks the Editorial Committee of Rubber Reviews for the honor of reviewing all the work that has been carried out at the Technische Hochschule, Hannover in the field of vulcanization. He welcomes the opportunity to limit the discussion chiefly to our own investigations. Since research on the vulcanization of rubbers is still in full swing and since our own investigations can on no account be considered as finished, it would certainly be premature to make the results of kinetic studies the subject of an exhaustive treatise. Then too, it happens that in the meantime several excellent critical papers have appeared, which give the state of our knowledge at the present time, and in which the questions come forth which are yet awaiting a solution in the realm of vulcanization. For such reviews we have to thank Farmer¹, who in 1946 published a monograph dealing particularly with the organic chemistry of vulcanization, and Craig², who, in his paper which appeared in 1957, dealt chiefly with the results of physicochemical and technological research on vulcanization. It therefore seems perhaps to be more appropriate

to report thoroughly for once, a portion of the field of vulcanization research together with repetition of a part of the experimental data, that is, to recount the kinetics of the chemical reactions which take place during vulcanization, and with which the Rubber Institute of the Technische Hochschule, Hannover, has been primarily concerned since its founding in 1951.

It is known that the results of kinetic studies are not always adequate to completely and uniquely clarify the mechanism of a chemical reaction in all details; for they are frequently ambiguous, and especially so when complex processes are involved. This holds—as will appear—for vulcanization reactions, and recommends caution in the interpretation and the theoretical treatment of experimental results. For here in particular next to nothing is known about the overall reactions; and the pertinent knowledge supplied by organic chemistry, instructive though it may be, is only of a qualitative nature.

Although studies of vulcanization kinetics are of great scientific and practical value, still the efforts of the physical and the organic chemists must supplement each other, so that some day it will be possible to present a complete picture of the vulcanization reactions. Kinetic studies of vulcanization with their quantitative results have always had technical significance. Indeed the logical understanding of the change in several characteristic aspects of the vulcanization process—in dependence on vulcanization time, temperature and concentration of the reactants which induce vulcanization—permits a general view of processes, which at this time are for the most part characterized through conventional technological tests rather than by a clear-cut measurement of the chemical transformations and exact physical quantities. Such a general view allows the interdependence of the processes to be recognized and their peculiarities to be disclosed. In other words, it is only in this way that the various phenomena which are observed in vulcanization reactions can be set in order and coordinated with the basic principals of our knowledge of the course of chemical reactions.

Such a goal can naturally be reached only if broad, systematic investigations are made, starting with relatively simple vulcanization reactions. Proceeding in this way is also necessary for reasons peculiar to the kinetic method.

It is well known that the calculation of an order of reaction, whether with respect to time or concentration, is an essential task in the evaluation of kinetic measurements, even though it is not always an easy one. It is possible to carry out the work with considerable accuracy, only when families of curves are available (temperature and concentration dependence of the reactions). But even then errors cannot be excluded, especially if we have no kind of hypothesis on which to build. Repetitions of measurements, which have sometimes made it necessary to correct our original results, are just as unavoidable as are checks and refinements of the explanations and interpretations of the findings. This is especially true when complex processes are involved for which the evaluation of experimental results can itself be a problem.

The discussion to this point thus presents our estimate of results at the present state of experimental work.

It will be necessary to introduce a section at the start of this paper which will recall to mind certain fundamentals of kinetics required for understanding the work, for it cannot be expected that every reader is familiar with this matter. This is understandable since kinetic studies in the field of vulcanization, even if they are sometimes carried out, are rather rarely consistently pursued.

II. FUNDAMENTALS OF KINETICS

We take note that for a reaction of the order n , we can express the rate by the equation:

$$dx/dt = k(a - x)^n \quad (1)$$

a —initial concentration of the reactant
 x —the reacted quantity of the reactant
 t —time
 k —rate constant
 n —order of the reaction

Equation 1 is the concentration-dependence of the rate, dx/dt ; hence n is the order of reaction with respect to concentration.

For $n = 0$ (reaction of zero order), we get from Equation 1:

$$dx/dt = \text{const.} \quad (2)$$

and the half-life time is proportional to the initial concentration of the reactant

Depending on whether $n = 1$ or some whole or fractional number either less than or greater than 1, the integration of Equation 1 gives two different expressions, which are known as the time laws.

For $n = 1$ (first order reaction) we have $dx/dt = k(a - x)$ and hence

$$\ln(a - x) = -kt + \ln a \quad (3)$$

and the half-life time ($x = a/2$) is constant, that is, equal fractions react in equal periods of time.

When $n \neq 1$, the integration of Equation (1) gives:

$$\left(\frac{1}{n-1} \right) (a-x)^{1-n} = kt + \left(\frac{1}{n-1} \right) a^{1-n} \quad (4)$$

or

$$\left(\frac{1}{1-n} \right) (a-x)^{1-n} = -kt + \left(\frac{1}{1-n} \right) a^{1-n} \quad (5)$$

and the half-life time becomes a function of the initial concentration:

$$\frac{2^{n-1} - 1}{(n-1)ka^{n-1}} = t_4 \quad (6)$$

If n has been accurately evaluated, then plots of $1/(1-n)(a-x)^{1-n}$, [when $n \neq 1$], or $\log(a-x)$, [when $n = 1$] against the time of reaction must give straight lines, from the slope of which the rate constant can be determined. In case of a zero order of reaction, the reaction curves themselves are straight lines.

When the reaction under consideration is a simple one, we generally find that the rate constants are independent of the initial concentration of the reactant being considered, and we recognize this if a family of parallel, straight lines is obtained when the results are plotted for various initial concentrations according to Equations 3, 4, or 5. In such cases, a straight line passing through

the origin is obtained when the initial rate, $(dx/dt)_0$, is plotted against the initial concentration raised to the n th power. Agreement then exists between the time law which has been found and the concentration dependence of the rate. This agreement is not always true especially in the case of complex reactions. In other words, there is a discrepancy in the order of reaction with respect to time and concentration. This is the case, for example, in the thermal decomposition of acetaldehyde, where the time law indicates a second order reaction whereas the initial rate increases with the $\frac{3}{2}$ power of the initial concentration of the aldehyde. According to Letort³, one of the reasons for such lack of agreement may be found in the effect of reaction products on the progress of the reaction. In particular, the time law has a smaller exponent, n , than the concentration-dependence of rate whenever the reaction product acts as a catalyst; when the reverse is true, it serves as an inhibitor of the process. In both cases the rate constant, as derived from the time law, becomes a function of the initial concentration of reactant. In the case of catalysis they will increase together and for inhibition the reverse must occur. In view of such relations, it is appropriate to differentiate, as Letort⁴ does, between order of reaction with respect to the time (n in the exponent of the time law) and order of reaction with respect to the concentration (exponent of the concentration dependence of the rate). The symbols n_t and n_c will be used for these respectively in what follows.

It is sometimes expedient to plot the results of experiments for which only fractional parts of the reactions occur:

If we use $(a - x) = c$ and $a = c_0$ in Equation 4, we have:

$$1/n - 1(c^{1-n} - c_0^{1-n}) = kt$$

From which, by a simple transformation, we have,

$$(c/c_0)^{1-n} - 1 = (n - 1)c_0^{n-1}kt$$

If we make $c/c_0 = \alpha$, we have the important relation:

$$\alpha^{1-n} - 1 = (n - 1)c_0^{n-1}kt \quad (7)$$

and we may introduce the dimensionless parameter $kc_0^{n-1}t \equiv \tau$ therein and have:

$$\alpha^{1-n} - 1 = (n - 1)\tau \quad (8)$$

Equation 8 was formulated by Powell⁵, and its graphic evaluation can serve to determine the order of reaction. It is readily seen that since $\log \tau = \log t + \log kc_0^{n-1}$, a simple plot of α against $\log t$ must give a characteristic curve for each value of n ; and curves with the same n value can be made to coincide by shifting one of them along the abscissa. To be sure, Equations 7 and 8 were used but little in the present work.

Equation 1 is used in another method for determining order of reaction. The differential quotients are secured for pairs of values which are as close together as is feasible along a reaction curve (concentration as a function of reaction time) and their logarithms are plotted against the corresponding concentrations. In case of a continuous order of reaction, a straight line results the slope of which gives the value of n .

The half-life time can also be used in determining the order of reaction, by means of Equation 6, for which we may write:

$$\log (2^{n-1} - 1)/(n - 1)k + (1 - n) \log c_0 = \log t_1 \quad (9)$$

If a whole set of reaction curves is available for different initial concentrations (c_0), then the log-log plot of half-life time against initial concentration must give a straight line with $(1 - n)$ as the slope; for the first term of the sum in Equation 9 is a constant. In this way we obtain directly the order of reaction with respect to concentration, that is n_c .

The method can also be used with a single reaction curve, by simply choosing tentatively two pairs of values, such as t_1 and c_0 as well as t_1' and c_0' and so on. Then we have:

$$\log t_1 = \text{const.} + (1 - n) \log c_0$$

and

$$\log t_1' = \text{const.} + (1 - n) \log c_0'$$

By subtracting one equation from the other and transforming, we have:

$$n = 1 + \frac{\log t'/t}{\log c_0/c_0'} \quad (10)$$

It is clear that use of this successive, systematic test with one or several reaction curves will give the order of reaction with respect to time and, accordingly, determine n_t .

The latter methods were used for the most part in the investigation here under consideration. Occasionally, however, the trial method was called upon. When, for example, we plot the experimental data according to a first order time law (Equation 3), and a reactant decreases along a curve which is concave to the time axis, it is clear that the reaction order must be less than 1; and, it must be greater than 1, if convex curves are obtained in this way. Take a case where a reaction order less than 1 is assumed, and it is certain that a zero order does not hold. Then we may try, for instance, if a straight line is obtained by plotting the data according to Equation 5 using $n = 0.5$. If the resulting curve is still concave, n must lie between 0 and 0.5, but if it is convex n must be greater than 0.5. By this method of trial the value for the reaction order which best fits the data can be found.

To obtain the activation energy we have confined ourselves throughout to the use of the equation of Svante Arrhenius, which defines the relationship between rate constant and temperature with adequate accuracy.

If Q_a = activation energy, we have:

$$d \ln k/dt = Q_a/RT^2,$$

and therefore:

$$\ln k = -Q_a/RT + C \quad (11)$$

Eliminating the integration constant C , substituting the calorie equivalent for R and introducing log to the base 10 in place of the natural logarithm, gives for the activation energy:

$$Q_a = \frac{(\log k_2/k_1)(4.576T_1T_2)}{(T_2 - T_1)} \quad (12)$$

Finally it should be mentioned, that the application of kinetic principles assumes precise analytical techniques. Attention must be paid to having good constancy of temperature for all measurements.

III. THE KINETICS OF VULCANIZATION PROCESSES

It is difficult to give a systematic classification of all vulcanization reactions if it should include all those for natural rubber as well as for the synthetic rubbers and also if it should be valid for all elastomers with the fundamental structure of a 1,5 polyene, as they are developed. An attempt might be made here now to differentiate between "direct" and "indirect" crosslinking reactions on the one hand and between elastomers with and without vinyl side groups. Thus, "direct" crosslinking or vulcanization is considered as taking place when the crosslinking reagent reacts directly with the rubber with formation of bridge bonds. We are dealing with an "indirect" crosslinking when the vulcanizing agent is used along with accelerators, activators and other chemicals in general which increase the rate of reaction between the particular rubber and the crosslinking reagent, or which increase the yield of crosslinks.

Chemicals which bring about direct crosslinking in all 1,5 polyenes are for example: sulfur, N,N'-tetrasubstituted thiuram disulfides as well as mixtures of monosulfides and sulfur corresponding to these disulfides in the presence of zinc oxide, peroxides such as dicumyl peroxide, dibenzoyl peroxide, di-*tert*-butyl peroxide and the like, aromatic di- and trinitro compounds, diazoamino compounds of the general structure $R-N=N-N=XR'$, and diazodicarbonic esters.

Chemicals which bring about a direct crosslinking only with 1,5 polyenes which have vinyl side groups are for example: several organic disulfides such as MBTS (benzothiazolyl disulfide), bisbenzimidazolyl disulfide and dithioglycolic acid diamide as well as sulfenamides.

The accelerated vulcanization of 1,5 polyenes by sulfur is at present actually the only example of an indirect crosslinking reaction. Used as accelerators are such compounds as organic bases, especially diphenyl guanidine and its derivatives, compounds of the thiuram series, xanthogenates, the ionic and complex salts of the N,N'-disubstituted dithiocarbamic acids, mercaptobenzothiazole and its disulfide, and sulfenamides. They are generally used along with zinc oxide, the addition of which is many times taken for granted, but which has little effect on the rate, but rather raises the level of the crosslinking.

The following sections will deal for the greater part with direct and indirect crosslinking of natural and synthetic rubber by sulfur and particularly with the kinetics of the concentration decrease of sulfur under the most varied conditions of temperature and concentration, and of the accelerator as well. As far as possible and to the extent to which the research has been carried out, the question of the changes which the accelerators undergo in the course of the vulcanization will also be quantitatively dealt with.

Two sections will deal with the direct crosslinking by peroxides, (dibenzoylperoxide and dicumylperoxide) as well as by thiuram disulfides. Since thiuram vulcanization shows a number of peculiarities, this section will also discuss vulcanizations by sulfur accelerated by members of the thiuram series, although these are actually indirect crosslinkings.

The kinetics of the crosslinking reactions which were studied and followed by measurements of the reciprocal equilibrium swelling or the modulus values is reserved for a special section. This is justified since a quantitative evaluation

of experimental data dealing with crosslinking encounters great difficulties. Along that line, it may be said that *measurements of slight degrees of crosslinking by means of swelling or modulus values*, of sufficient accuracy for purposes of kinetic interpretation, are at present practically impossible. Finally, the determination of end values of crosslinking for systems which show reversion is altogether problematic and uncertain. This brings to mind the fact that the relation between the number of crosslinks (bridge bonds) and swelling is established by the theory of Flory and Rehner and in our opinion it is not certain that the ideas developed by these authors can be used in connection with sulfur vulcanizates. It will therefore be more correct if we confine ourselves at first to a more qualitative discussion of curves which describe the course of the crosslinking in order to investigate with which partial reaction the crosslinking correlates.

A. THE DIRECT VULCANIZATION BY SULFUR, REACTION OF SULFUR WITH NATURAL AND SYNTHETIC RUBBER

The reaction of sulfur, especially with natural rubber, has been the subject of many kinetic studies⁶⁻¹¹ in the past. Springer¹² has assembled and discussed the work published up to 1945, and in doing this has attempted to clear up the apparent contradictions which appear in that literature. Craig², as already mentioned, undertook a similar critical analysis in 1957. We find the view to be predominant that sulfur reacts according to a time law of zero order for a greater part of the range of concentration, whereas the concentration dependence of the rate indicates a reaction order between 0.8 and 1.0. However, Lewis, Squires, and Nutting¹³ pointed out in 1937, that there are three characteristic curves for the sulfur decrease, one principally in the low ranges of initial sulfur concentration with convex curvature to the time axis, another at very high concentrations, first with a concave curvature, eventually reaching a point of inflection and passing into the convex type, then a third curve found in the medium concentration range which, in our opinion, shows a course for the concentration decrease which is nearly a reaction of zero order. This state of affairs shows up also in measurements by Skellon¹⁴ and was discussed not long ago by Craig² in support of interpretations made by Nordlander¹⁵. It must be considered quite out of the question for such observations to be incorrect; rather we may say that they are the expression of a very complicated kinetics, which responds perhaps very sensitively to impurities in the rubber. However, judging from past experience, it is probably correct, to say that the decrease of sulfur is characterized by lack of agreement between the time law (n_t) and the concentration dependence of the rate (n_c), which van Iterson¹⁶ has rightfully considered as evidence of autocatalysis.

Because reliable information on the reaction of sulfur with rubber must also be of significance in clarifying the kinetics of accelerated vulcanizations, we studied afresh the concentration decrease of sulfur in rubber under various conditions of temperature and initial sulfur concentration. Several synthetic rubbers were also included in order to study, among other things, the effect of chemical constitution of the elastomer on sulfur decrease. These studies are by no means finished, yet the results which are already extensive may be presented here along with the attempt to explain them¹⁷.

1. *Decrease of concentration of sulfur in its reaction with natural rubber.*—We studied the decrease of sulfur at different concentrations and temperatures with two raw rubbers (pale crepe) from different sources. The starting material

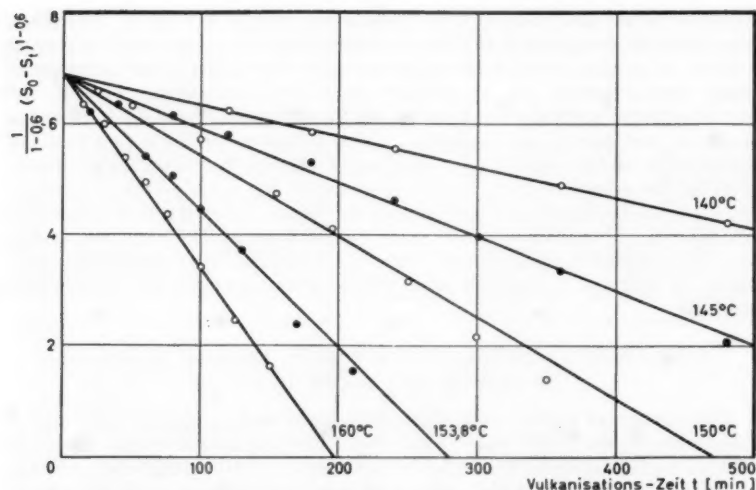


FIG. 1.—Decrease of sulfur according to the time law with $n_t = 0.6$ at various temperatures (reaction of natural rubber with sulfur). Zeit = time.

was always thoroughly extracted with acetone to free it from the bulk of impurities (resins, proteins, etc.).

For the quantitative determination of the sulfur that was still uncombined in the vulcanizates, the samples were extracted in the cold with a benzene/alcohol mixture, (2:1). The solvent was repeatedly renewed and the extraction was completed in about 8 days. The collected extracts were combined.

In the experiments of Series 1, portions of the extracts, made up to a certain volume after evaporation of the solvent, were treated with a solution (25%) of

TABLE I
RATE CONSTANTS FOR SULFUR DECREASE IN SOME 1,5 POLYENES AT
VARIOUS TEMPERATURES

$1/T$ $\times 10^3/K$	T in $^{\circ}C$	Natural rubber (S_0) ₀ = 12.5 mmole $K \cdot 10^6$		Natural rubber (S_0) ₀ = 12.5 mmole + ZnO $K \cdot 10^6$		NBR (S_0) ₀ = 10 mmole $K \cdot 10^6$		cis-1,4 poly- butadiene (S_0) ₀ = 10 mmole	
		mmole ^{0.4} Series 1	min ⁻¹ Series 2	mmole ^{0.4} min ⁻¹	mmole ^{0.5} min ⁻¹	mmole ^{0.4} Series 1	min ⁻¹ Series 2	$t_{1/2}$ min	$t_{1/4}$ min
2.54	120		0.63					7980	4980
2.51	125					1.31			
2.48	130		1.79			1.90		2770	1710
2.45	135		3.33			3.16	3.40	1812	1015
2.42	140	5.50	5.43	5.8	7.25	4.98	5.80	1200	703
2.39	145	9.70	8.33	10.3	12.50	8.84	10.10	720	414
2.36	150	17.50	14.28	16.5	19.5	13.21	16.95	396	222
2.34	155	24.50		28.0	32.5				
2.31	160	35.10		46.7	53.0				
n_t		0.6	0.6	0.6	0.5	0.6	0.6	concave	
Q_A in kcal/ mole		35	33.8	37.1	35.4	33.2	35.6	33.0	

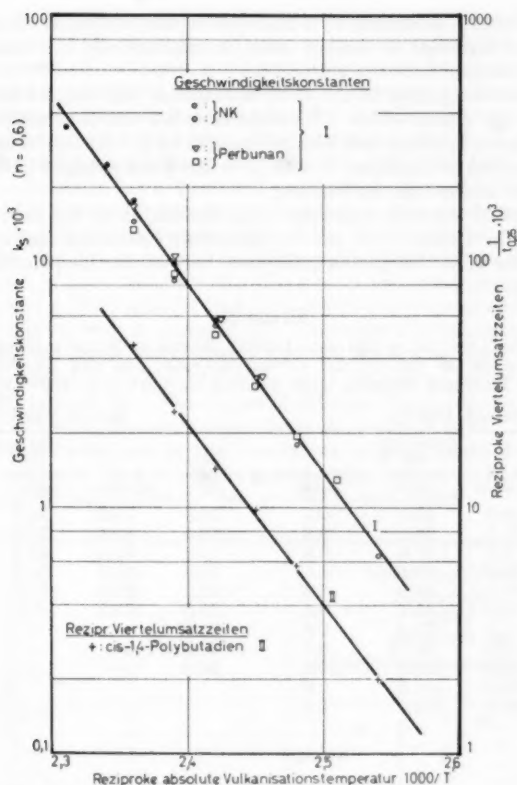


Fig. 2.—Temperature function of the rate constants for sulfur decrease ($n_1 = 0.6$) in natural rubber and NBR (Perbunan) (I) as well as quarter-life times for *cis*-1,4 polybutadiene (II). Geschwindigkeit = velocity, NK = natural rubber, Viertelumsatzzeit = quarterlifetime.

sodium sulfite and heated at the boiling point for several hours. This converted the free sulfur to an equivalent amount of thiosulfate. After addition of an excess of formalin (40%), the solution was acidified with acetic acid and titrated with iodine solution¹⁸.

In Series 2, the extract was warmed for some time with excess of a solution of potassium cyanide. This converts all the sulfur to thiocyanate. The excess of cyanide was destroyed by addition of $N/10$ acetic acid and the solution dried completely under vacuum. The residue was then taken up in water and the aqueous solution titrated conductometrically with silver nitrate¹⁹.

The results obtained by the two methods are in good agreement, as we determined to our satisfaction in preliminary experiments.

a. *Temperature dependence of the rate of sulfur decrease.*—In order to determine the dependence of the rate of sulfur decrease on temperature, rubber compounds were used in both series of experiments which contained 12.5 mmole $S_8/100$ g or 3.2 g sulfur per 100 g of rubber. The reaction curves were in every case convex to the time axis regardless of temperature. A plot of the

experimental results according to a time law of the first order showed beyond doubt that the exponent in the law must be substantially less than 1; that is, n_t must be a fraction between 1 and zero.

Accurate determination of the order of reaction with respect to time gave a value of $n_t = 0.6$ in both series. That the time law was accurately determined is shown in Figure 1, which uses results from Series 1. As can be seen, plotting the data according to Equation 5 with $n_t = 0.6$ gives straight lines at all temperatures; this is also true for Series 2.

Calculation of the rate constants from the slopes of the curves gives the values shown in Table I. It can be seen that somewhat higher values are found for Series 1, but no great significance may be ascribed to this.

TABLE II
RATE CONSTANTS ($n_t = 0.6$) AND INITIAL RATES OF SULFUR DECREASE IN
DEPENDENCE ON THE INITIAL CONCENTRATION, FOR THE REACTION OF
NATURAL RUBBER WITH SULFUR AT 145° AND 150° C

Series 1, (150° C)				Series 2, (145° C)			
(S ₀) ₀ mmole/ 100 g	$k \cdot 10^3$ ($n = 0.6$)	$[d(S_0)/dt]_0$ $\cdot 10^3$ mmole $\cdot \text{min}^{-1}$	Curve type and n_t	(S ₀) ₀ mmole/ 100 g	$k \cdot 10^3$ ($n = 0.6$)	$[d(S_0)/dt]_0$ $\cdot 10^3$ mmole $\cdot \text{min}^{-1}$	Curve type and n_t
3.125	10.0	19.8	0.6	10.0	7.46	29.7	0.6
4.6875	11.5	29.1	0.6	12.5	8.33	37.9	0.6
6.25	12.5	37.5	0.6	15.0	8.54	43.4	0.6
7.8125	13.7	47.1	0.6	20.0	10.48	63.2	0.6
9.375	14.5	55.5	0.6	22.5	12.28	(79.5)	0.6
10.9375	15.5	65.1	0.6	25.0	13.45	(92.8)	0.6
12.5	17.5	79.5	0.6	30.0	—	—	S-shape
15.625	18.6	96.78	0.6	40.0	—	—	
18.75	20.0	116.2	0.6	50.0	—	—	
21.875	21.4	136.3	0.6				
25.0	23.0	159.0	0.6				
37.5	—	—	S-shape				
50.0	—	—					
62.5	—	—					
75.0	—	—					

By plotting the log of the rate constant against the reciprocal of the absolute temperature we got two straight lines lying close to each other and with practically the same slope, Figure 2. The activation energy calculated from Series 1 is 35 kcal/mole, and from Series 2 is 34 kcal/mole. This is good mutual agreement and is in good agreement with the statements in the literature²⁰. Hence we cannot assume that the activation energy is dependent on the concentration.

It is known that metal oxides, especially zinc oxide, exert a marked influence on the physical properties of vulcanizates; they bring about improvements. Hence we investigated whether or not the addition of zinc oxide would change the kinetics of the reaction of sulfur with rubber.

Measurements (in Series 1) in the presence of zinc oxide (50 mmole = 4.07 g/100 g compound) and with an initial concentration of sulfur of 12.5 mmole S₈ in 100 g, showed that the concentration decrease followed curves which were convex to the time axis. It was possible in this case, to construct reaction curves just as well according to a time law with the exponent $n_t = 0.6$ as with $n_t = 0.5$. The rate constants calculated from these time laws are also given in Table I. We find very good agreement if we compare these values calculated

for $n_t = 0.6$ with those calculated for vulcanizations in the absence of ZnO and for $n_t = 0.6$. In the case of rate constants calculated for $n_t = 0.5$, which of course must be larger, good comparison is no longer possible because of the different exponents of the time laws. However, we may say that zinc oxide has no appreciable effect on the kinetics of sulfur decrease, either qualitatively (exponent of the time law) or quantitatively (rate).

b. Concentration dependence of the rate.—Of course the fact that the time law for sulfur decrease has a fractional exponent leads to the thought that we are dealing with a complex process, in which case it becomes more important to undertake a systematic investigation of the dependence of rate on concentration. This was also important for this reaction because two questions must be cleared up: (1) does the character of the reaction curves change with initial concentration of sulfur? and (2) how is it possible to express such a change in the shape of the curve if it is observed? Therefore the decrease in concentration of sulfur was measured in Series 1 at 150°C in the range from 3.125 to 75 mmoles S_8 and in Series 2 at 145°C by raising the initial sulfur concentration from 10 to 50 mmoles S_8 . The choice of different temperatures permitted an examination of the temperature dependence at the same time.

As the results obtained in both cases are in good qualitative agreement (Table II), we give in Figures 3 and 4 only the reaction curves found in Series 1, since the range of concentrations was greater in this series.

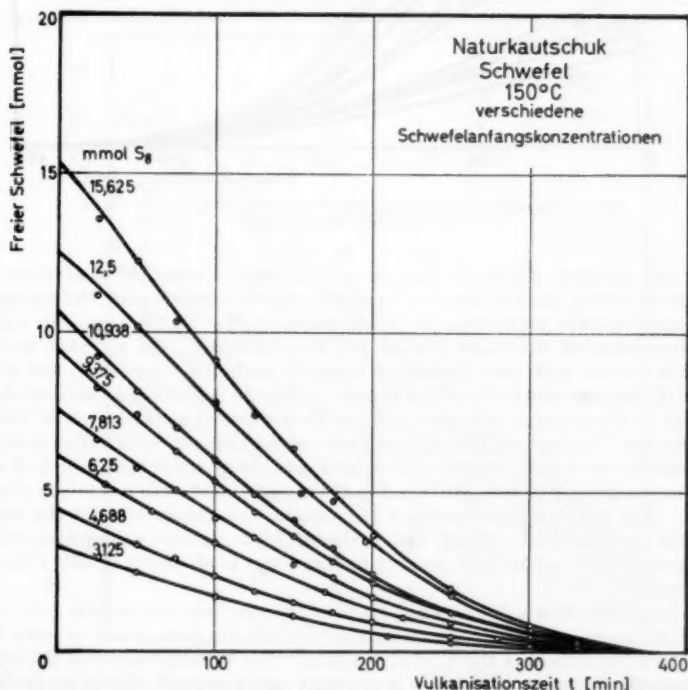


Fig. 3.—Decrease of sulfur concentration in natural rubber at 150°C and various initial concentrations. Verschiedene = various, anfangs = initial, freier = free.

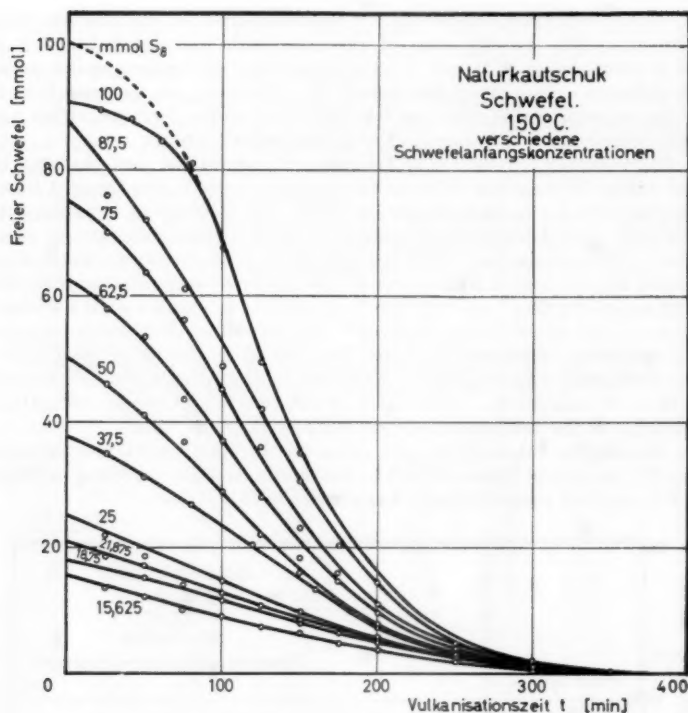


FIG. 4.—Decrease of sulfur concentration in natural rubber at 150°C and various initial concentrations.

It can be seen, Figure 3, that up to an initial concentration of about 10 mmoles S_8 /100 g, the reaction curves are convex to the time axis; but at higher concentrations the curves become concave to that axis, Figure 4, and the higher the concentration the more pronounced the curvature. So we have normal reaction curves, with rate decreasing regularly over the time range, and those in which the rate rises in the initial region—probably indicating an autocatalytic process in the decrease of sulfur. Thus we confirm the statements of Lewis, Squires and Nutting¹³, in which three types of reaction curves of sulfur decrease will exist in the region between the convex and the concave type which at any rate for the greater part of the reaction are in agreement with a reaction of zero order. For the kinetic analysis of the results, this means that in the initial reaction region we are dealing with a change from positive to negative values of the order of reaction with respect to time; this is of course chiefly a formal statement.

It is obvious that a kinetic analysis of all the reaction curves must meet with many obstacles, yet the determination of the half-life time shows at once that this value, regardless of the type of reaction curve is independent of the initial concentration of sulfur and hence is constant in this respect; this holds for both series of experiments and is also true when zinc oxide is present. We must

infer from this that the dependence of the rate of sulfur decrease on concentration will follow a first order reaction. That should also be concluded from the dependence of the initial rate on concentration, but the time law must be known to enable us to show this.

For calculations thereof, we confined ourselves to a closer study of the reaction curves which were convex or at least convex for the greatest part of the reaction, as they obviously tend to appear in the range of relatively low or medium concentrations. Thus we abandoned the closer study of the curves corresponding to the autocatalytic process of sulfur decreases.

It was found that the convex curves of Series 1 for concentrations ranging from 3.125 to about 25 mmols S_8 could be represented quite accurately by the time law with the exponent $n_t = 0.6$ for the greatest part of the range of reaction. Figure 5 shows that straight lines are obtained when the data are plotted according to Equation 5. Yet it is clear that the curves, for $t = 0$, do not intersect the ordinate at the calculated initial values. This merely indicates that there must be some initial slight concave curvature. And now according to these exploratory studies, since the convex portions of the S-shaped reaction curves at higher sulfur concentrations as they appear after passing through the point of inflection, obey a time law with the exponent $n_t = 0.6$, we have the following situation.

With increasing sulfur concentration, there occurs a continuous transition from a normal reaction curve, convex to the time axis, to one in which the

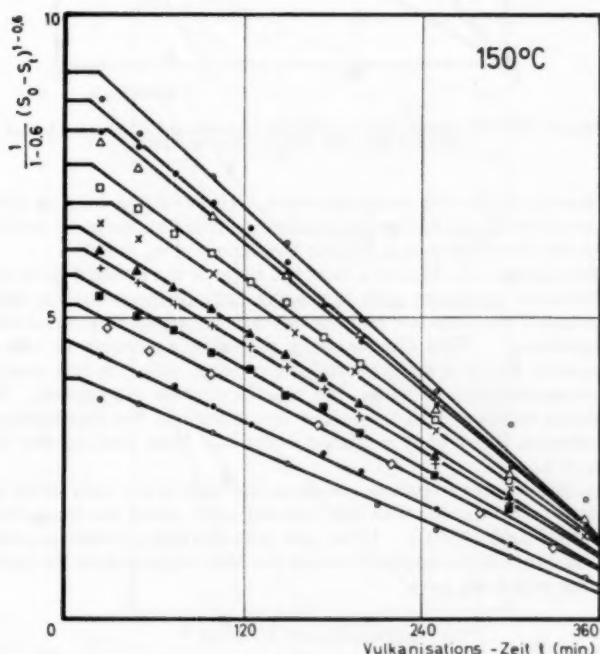


Fig. 5.—Decrease of sulfur concentration in natural rubber at 150° C according to the time law with $n_t = 0.6$ (various initial concentrations); compare Table II.

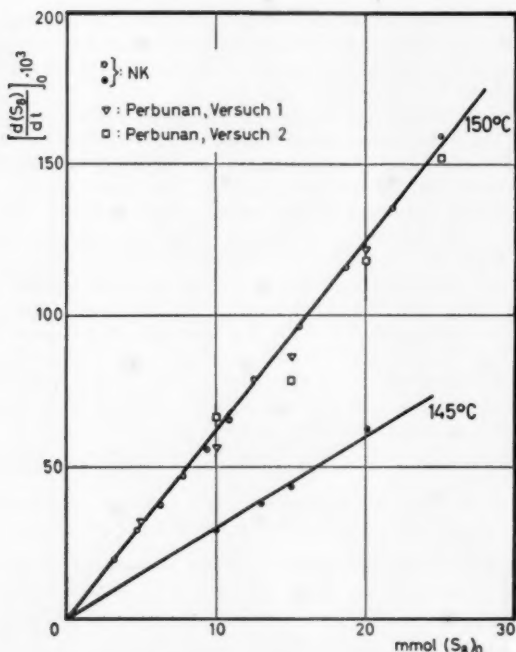


FIG. 6.—Relation between initial rate of sulfur decrease and initial concentration (reaction of S_8 with natural rubber or NBR).

S-form becomes more and more apparent. However, as long as the convex type exists either for all or for the greatest part of the range of reaction, it is found that the time law which fits has the exponent $n_t = 0.6$.

It is also apparent in Figure 5, that the slope of the straight lines and hence the rate constant increases with increasing initial concentration; this should not be the case if the time law and the dependence of the rate on concentration were in agreement. This disagreement indicates, according to Letort³, that the decreases in sulfur is an autocatalytic process, which is true even for that range of concentrations in which the reaction curves are convex. Since the rate constants increase with increasing concentration, the dependence of rate on concentration must obey a higher order law than that of the time law, that is, $n_c > n_t$.

The calculated rate constants are given in Table II for both series of experiments. It should be noted that they cannot agree, since the temperatures are different (150° and 145°C). If we put corresponding initial concentrations and rate constants in the applicable time law then we calculate the initial rates, Table II, for which we have

$$[d(S_8)/dt]_0 = k' \cdot (S_8)_0^{0.6} \quad (13)$$

Thus, k' is the rate constant which is dependent on sulfur concentration.

Figure 6 shows that a plot of the initial rates against initial sulfur concentrations give a straight line through the origin and this confirms what was already inferred from the constancy of the half-life times, which was emphasized above, namely that the dependence on concentration of the rate of sulfur decrease exhibits a reaction of the first order, or that $n_c = 1$; and because $n_t < n_c$, the discrepancy between time law and concentration dependence of the rate, indicates, according to Letort³, a catalysis brought about by the reaction products.

When we consider the fact that the dependence of rate on concentration is much more important for our understanding of the nature of a chemical reaction than the time law we could be content with the results showing that decrease in sulfur without doubt follows a first order reaction, but we would still have to decide, if we were dealing with homolysis or a pseudomonomolecular reaction (structural units of the rubber in excess). If the homolytic breaking of the S_8 ring in the reaction of sulfur with rubber is the rate-determining step, then we should expect the rate of sulfur decrease to be essentially the same in all rubbers. Although Craig² indicates that this is not the case, we nevertheless studied the kinetics of the reaction of sulfur with several synthetic elastomers, namely NBR (Perbunan), *cis*-1,4 polybutadiene, and *cis*-1,4 polyisoprene.

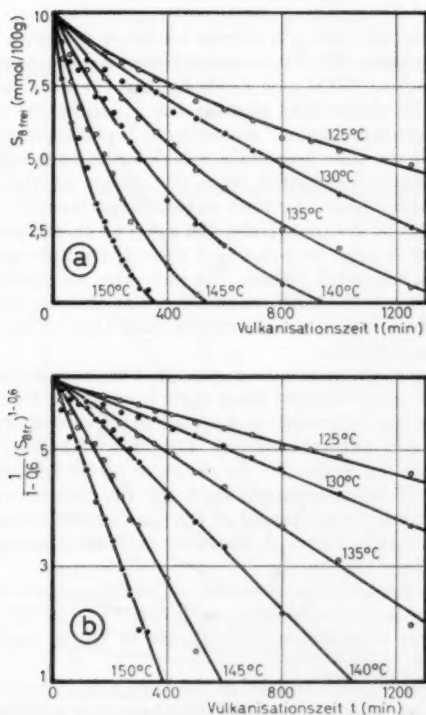


Fig. 7.—Concentration decrease of sulfur in NBR at various temperatures, (a), and according to the time law with $n_t = 0.6$, (b). $[(S_8)_0 = 10 \text{ mmoles/100 g of compound}]$. fr = frei = free.

Moreover, perhaps the question of why the reaction curves change shape with the initial concentration of sulfur could be answered in this way.

2. *Decrease of sulfur concentration in its reaction with synthetic rubbers.*—The *cis*-1,4 polybutadiene, which was used contained about 2 to 4% of vinyl side groups which resulted from 1,2 addition in the polymerization. It was not to be supposed, however, that this would qualitatively affect the kinetics of the sulfur decrease. The stabilizer, a dialkylphenol dimerized by condensation with formaldehyde, could be removed by extraction. The product was studied both as received and after extraction.

The NBR (copolymer of butadiene and acrylonitrile)—with a considerably higher vinyl side group content—contained a basic stabilizer, which was removed by exhaustive extraction with methanol. Yet we should assume that the extracted elastomer—especially when the raw product was stored some time—was never free of impurities. It could be vulcanized by heating (peroxide containing); the vulcanizates were always dark in color.

The determination of sulfur in the vulcanizates was done by the thiocyanate method which was described previously (III, A, 1).

a. *The temperature dependence of the rate.*—The sulfur decrease in the case of Perbunan was first studied at different temperatures in two series of experiments. The initial sulfur concentration was held at 10 mmoles/100 g throughout.

Figure 7a shows the reaction curves obtained in Series 1. They are all convex to the time axis. The exponents for the time law were also found to be $n_t = 0.6$ in this series. This also holds for the curves of the same shape in Series 2. Figure 7b shows that plotting the experimental results in a graph which corresponds to this time law according to Equation 5 yields straight lines. This indicates that the time law which was determined is well satisfied.

The rate constants calculated from the slopes of the straight lines in Figure 7b are listed in Table I for both series of experiments. They are in good mutual agreement and are practically the same as those found in Series 1 for natural rubber, but it must be noted that there the sulfur concentration, being at 12.5 mmoles S_8 , was a bit higher. At any rate, we may conclude that the rate of sulfur decrease in the NBR studied here was of about the same magnitude as in natural rubber, but it should not be said that a highly purified NBR would give the same results.

Plotting the log of the rate constant against the reciprocal of absolute temperature, Figure 2, gives straight lines quite accurately, from whose slope the activation energies are calculated and found to be essentially the same as for the sulfur decrease in natural rubber. They are 33.2 kcal/mole for Series 1 and 35.6 kcal/mole for Series 2. In the case of *cis*-1,4 polybutadiene, only reaction times could be determined, since the reaction curves always had an S-shape. By plotting the reciprocal of the quarter-life times against $1/T$, we got the straight line II in Figure 2; the same activation energy as with natural rubber is derived from its slope.

b. *Dependence of rate on concentration.*—The dependence of rate on the concentration was studied in both Series with NBR at 150° C. The initial concentrations of sulfur were set at 5, 10, 15, 20, or 15, 20, and 25 mmoles S_8 in 100 g of compound.

The reaction curves were convex to the time axis in every case. Thus the convex type of curve held for the NBR used here over a rather extensive range of concentrations. Thus far we have not yet investigated whether concave reaction curves would finally occur with still higher sulfur concentrations. At

TABLE III
RATE CONSTANTS AND INITIAL RATES OF SULFUR DECREASE IN
NBR AT 150° C

Series 1 (150° C)				Series 2 (150° C)			
$(S_0)_0$, mmoles/ 100 g	$k \cdot 10^3$ ($n=0.6$)	$[d(S_0)/dt]_0$ $\cdot 10^3$	n_1	$(S_0)_0$, mmoles/ 100 g	$k \cdot 10^3$ ($n=0.6$)	$[d(S_0)/dt]_0$ $\cdot 10^3$	n_1
5	12.0	31.6	0.6				
10	14.2	56.7	0.6				
15	17.0	86.2	0.6	15	15.32	77.8	0.6
20	20.3	122.3	0.6	20	19.54	118.0	0.6
				25	21.9	151.0	0.6

any rate, the curves are still convex at 40 mmoles S_0 , as we found in exploratory experiments.

It was again found that the half-life times were practically constant in both series of experiments and results are found in this respect which are like those for natural rubber. So we may conclude from the work done with this NBR that the dependence of rate of sulfur disappearance on concentration follows a first order law even though the product was certainly not entirely pure.

This has shown that for the ranges of concentration used in the two series of experiments, the decrease in sulfur concentration again can be described by a

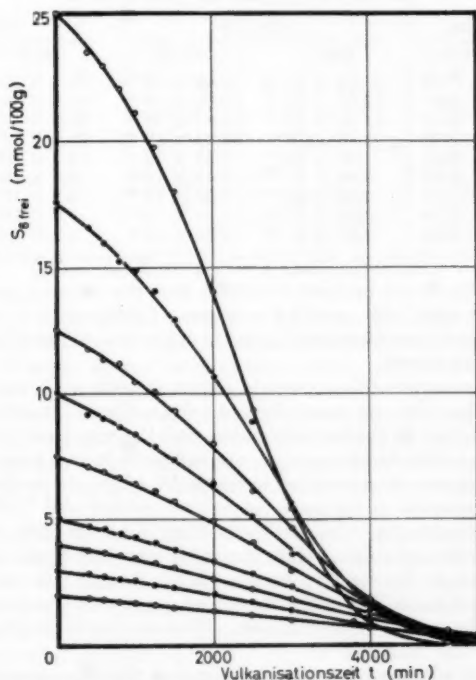


Fig. 8.—Decrease of sulfur concentration in *cis*-1,4 polybutadiene at 130° C and various initial concentrations.

time law with exponent $n_t = 0.6$; and when we substitute corresponding initial concentrations and rate constants in the time law, then we calculate the values of initial rates given in Table III. Plotting these values against the initial concentrations of sulfur also gives a straight line; passing through the origin, Figure 6; in other words, we get the same results as in the reaction of natural rubber with sulfur: the concentration dependence shows a first order course.

With *cis*-1,4 polybutadiene the dependence of the rate of sulfur decrease on the concentration was studied at 130° and 150° C with 2, 3, 4, 5, 7.5, 10, 12.5, 17.5, and 25 mmoles S_8 per 100 g compound. Similar results were obtained at both temperatures. Figure 8 gives the reaction curves for the measurements made at 130° C.

It can be seen that only concave curves are obtained with this elastomer over the whole range of concentrations. Since the unextracted product, with the inhibitor present, was used in these experiments, we thought that this may have an effect on the shape of the reaction curves. Yet we get the same curves when the inhibitor has been removed. *We have the impression that this cis-1,4 polybutadiene is at present the elastomer which is best suited for fundamental studies, and that it is probably the purest product, when well extracted, that we have*

TABLE IV
HALF-LIFE TIMES AND INITIAL RATES FOR THE REACTION OF
cis-1,4 POLYBUTADIENE WITH SULFUR

(S ₈) ₀ , mmoles/ 100 g	<i>t</i> _{0.5} , min		[d(S ₈)/dt] ₀		[Δ(S ₈)/Δ <i>t</i>] _{max}	
	150° C	130° C	150° C	130° C	150° C	130° C
20	274	2170	23.08×10^{-3}	27.00×10^{-4}	84.4×10^{-3}	94.0×10^{-4}
17.5	294	2380	18.57×10^{-3}	19.90×10^{-4}	40.8×10^{-3}	54.0×10^{-4}
12.5	310	2520	13.38×10^{-3}	15.40×10^{-4}	26.0×10^{-3}	33.5×10^{-4}
10.0	327	2480	8.10×10^{-3}	13.30×10^{-4}	21.5×10^{-3}	25.7×10^{-4}
7.5	327	2640	7.80×10^{-3}	8.55×10^{-4}	14.1×10^{-3}	19.5×10^{-4}
5.0	347	2760	6.08×10^{-3}	7.15×10^{-4}	9.5×10^{-3}	10.5×10^{-4}
4.0	356	2750	4.94×10^{-3}	5.40×10^{-4}	6.8×10^{-3}	8.8×10^{-4}
3.0	385	2770	3.33×10^{-3}	4.36×10^{-4}	5.0×10^{-3}	6.5×10^{-4}
2.0	367	2900	2.82×10^{-3}	3.34×10^{-4}	3.2×10^{-3}	4.0×10^{-4}

thus far used. So we are inclined to believe that the concave curve will be the prevailing type with fully purified rubbers. Certainly the vulcanizates of purified *cis*-1,4 polybutadiene are lighter in color than those of natural rubber, which are reddish brown.

The kinetic analysis of the curves in Figure 8 meets with several difficulties, for an overall time law can naturally not exist. Hence we confined ourselves to the determination of the half-life times, and the graphical determination of the initial rates which, in our opinion, are sufficient to recognize the essentials. The pertinent figures are assembled in Table IV which shows that the half-life times are not constant as they are for natural rubber and NBR, but show a trend with concentration. In particular, they decrease with increase in the initial concentration of sulfur, while the rates correspondingly increase at the point of inflection of the concave curves, $(\Delta(S_8)/\Delta t)_{\max}$. In connection therewith, we find that the initial rate, determined graphically, increases only as the 0.9 power of the initial concentration. This is shown in Figure 9 for the experiments at 130° and 150° C.

Thus we find with *cis*-1,4 polybutadiene that the dependence of the rate of sulfur decrease on concentration does not accurately follow a first order process.

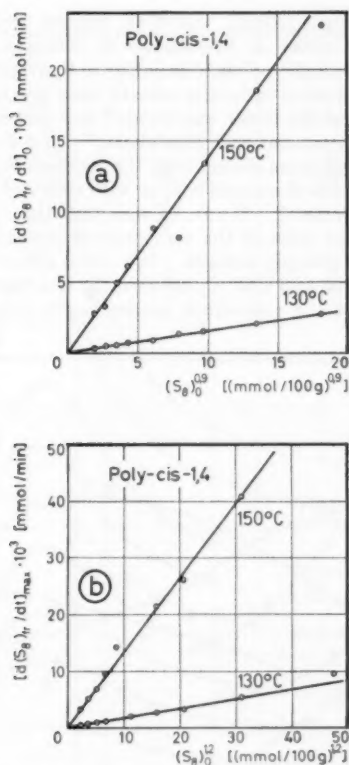


Fig. 9.—Relation between initial rate (a) as well as maximum rate (b) and initial sulfur concentration at 130° and 150° C (*cis*-1,4 polybutadiene).

However, we may not conclude from this that there is a fundamental difference between natural rubber and *cis*-1,4 polybutadiene with respect to the character of the sulfur decrease during their vulcanization. When the corresponding half-life times for sulfur decrease are compared, we find of course that there is a great difference between natural rubber and *cis*-1,4 polybutadiene. The rate of sulfur decrease with natural rubber is indeed substantially greater than with *cis*-1,4 polybutadiene. This reduces the plausibility of the assumption that homolysis of the S_8 ring is the rate determining step in the reaction of sulfur with rubber.

3. *The polysulfide bound sulfur in the reaction of natural and synthetic rubber with sulfur.*—Sections III, A-1 and -2 dealt only with the kinetics of the decrease in sulfur concentration. Before the results are discussed, it will be appropriate to examine the formation of polysulfide bound sulfur, which is always observable, and try to see what connection there may be between it and the decrease in sulfur concentration.

To determine the portion of sulfur bound as polysulfides, the vulcanizates were first extracted with a mixture of alcohol and benzol to remove the free

sulfur. The remaining material was then treated with lithium aluminum hydride in dry ether under an atmosphere of nitrogen. This process, after acidification, changes all the polysulfide sulfur to hydrogen sulfide. The latter was passed into a solution of cadmium acetate, thus precipitating an equivalent of cadmium sulfide and the latter was titrated iodometrically²¹.

It was found, in agreement with Studebaker²², that the polysulfide sulfur in every case goes through a maximum with the reaction time. This is shown in Figure 10 using reactions of natural rubber with sulfur at various temperatures in the experimental Series 2. It can be seen that the maxima move into the area of shorter reaction time as the temperature increases, and that they become more and more sharply defined. We could not reach the maximum in the experiments at 120° and 130° C, because the reaction times were too long. The curves show that the polysulfide sulfur finally does not decay again to

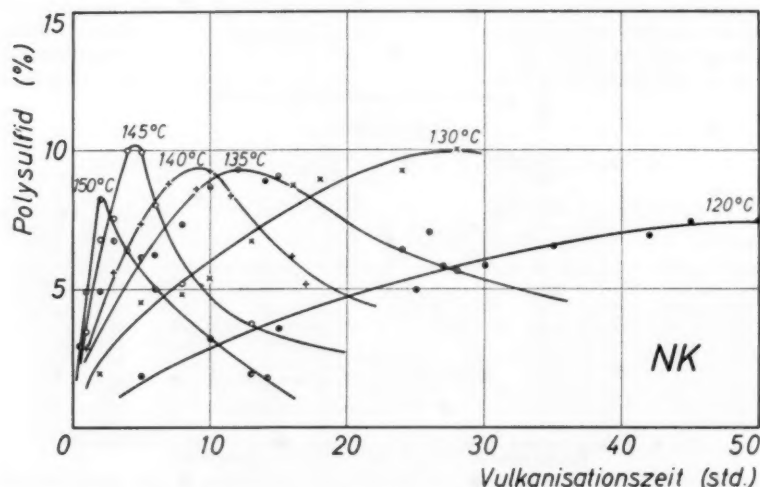


FIG. 10.—Dependence of polysulfide combined sulfur on the temperature (reaction of S_8 with natural rubber; $(S_8)_0 = 12.5$ mmoles on 100 g compound). std = hours.

zero, and this of course is shown better when the reactions are followed over longer periods of time (see Figure 11). The curves of Figure 10 do not really let us decide if the maximum polysulfide content is dependent on temperature; the maximum portion of the sulfur as polysulfide in this series of experiments was 10% of the total sulfur used.

There is an unmistakable dependence of the maximal polysulfide content of the vulcanizates, on the initial concentration of sulfur. This is shown in Figure 11, where the polysulfide sulfur in mmoles S_8 is plotted against the reaction time for different sulfur concentrations. It will be noted that the curves are displaced a certain distance along the ordinate, to prevent overlapping.

We can see that more and more polysulfide is formed with increasing initial concentrations. While a maximum of 0.8 mmole = 8% was found when $(S_8)_0$ was 10 mmoles, the corresponding value was 6.8 mmoles = 13.6% when $(S_8)_0$ was 50 mmoles. The increase and decrease of polysulfide sulfur both follow

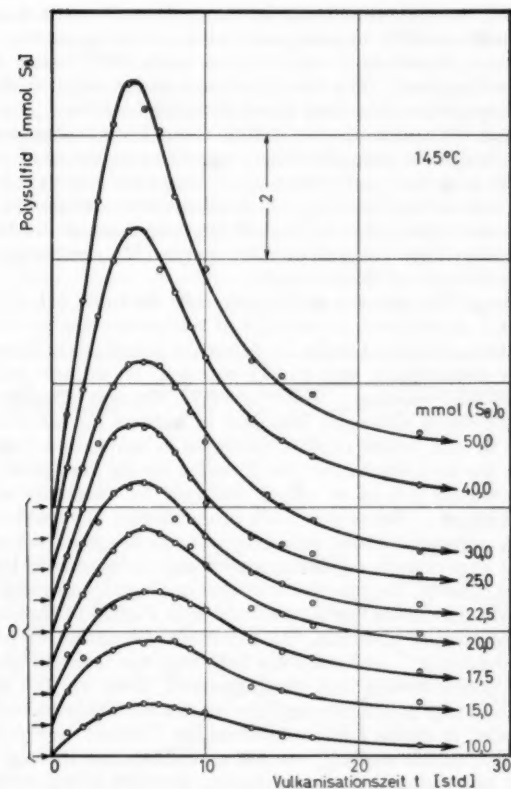


FIG. 11.—Relation between polysulfide combined sulfur and reaction time at 145° C and various initial concentrations (S_8 with natural rubber).

along normal reaction curves; that is along concave curves (to the time axis) for increase and along convex curves, for decrease. This is not always the case; for example, curves for polysulfide formation have been observed for the reaction of *cis*-1,4 polybutadiene with sulfur, in which the maxima are very sharp and they are flanked by convex curves. This may probably be associated with the concave curves for sulfur decrease which are noted for this elastomer over the whole range of concentration. It is not at all impossible that such curves for the formation and disappearance of polysulfides may also hold for natural rubber if very high initial concentrations of sulfur are used, and particularly if the work is done at higher temperatures. The results are complicated, but may possibly be explained qualitatively by the assumption that two opposing factors determine the course of the polysulfide content.

The polysulfide content of different rubbers varies widely, Perbunan vulcanizates contain surprisingly little polysulfide; for instance only about 1% of the initial concentration when $(S_8)_0 = 10$ mmoles. Evidently the poly-

sulfide destroying reaction runs faster in this polymer than it does in natural rubber. This may possibly be associated with a reaction on the part of the vinyl side groups. However, it may depend upon NBR being more highly polar than natural rubber. The vulcanizates of *cis*-1,4 polybutadiene contain substantially more polysulfide than those of natural rubber. For $(S_8)_0 = 10$ mmoles we find at the maximum about 20% of the initial concentration which is two times the value for natural rubber. In this case we must suppose that the polysulfide is destroyed more slowly than in natural rubber. It is remarkable that in the case of butyl rubber, which is known to contain but little of the isoprene comonomer, the sulfur at least at the beginning of reaction is found exclusively as polysulfide. Apparently the polysulfide destroying reaction is blocked here by the lack of double bonds.

4. *Discussion of the experimental results.*—In Sections III A-1 and -2 it appeared that the dependence of the rate of sulfur decrease on concentration indicates a reaction of the first order, so either the homolysis of the sulfur molecule is the rate determining step in the reaction, or we are dealing with a pseudomonomolecular reaction. Since, however, the rate of sulfur decrease in *cis*-1,4 polybutadiene is distinctly less than in natural rubber, the homolytic breaking of the S_8 ring, which is often discussed in connection with vulcanization, cannot be the deciding factor; for if that were the case then the rates of sulfur decrease should not be so widely different for reactants which are so similar in constitution. Hence it is more probable that the reaction of rubber with sulfur is a bimolecular one, which appears to be pseudo-monomolecular because there is always such a great excess of elastomer present in the experimental reactions; that is, the reaction is of the first order with respect to sulfur.

It is shown by the curves for natural rubber in Figure 11 that regardless of the initial concentration of sulfur, the maximum formation of polysulfide is reached in about 6 hours. And while the half-life times for sulfur decrease were independent of concentration and were constant, these are the times within which the maximum for polysulfide appears; and when the initial rates of sulfur decrease calculated in Series 2 for natural rubber (Table I) are plotted against the maximum polysulfide content, we get a straight line through the origin. This is a result expressing the proportionality between initial rate and initial concentration of the sulfur, Figure 6. Finally, according to previous studies, there exists an approximate proportionality between the initial rate of polysulfide formation, as determined by graphical methods, and the initial concentration of sulfur; this was shown in studies made with *cis*-1,4-polybutadiene.

This leads to the inference of a close relationship between sulfur decrease and polysulfide formation, and when we consider that sulfur is bound almost exclusively as polysulfide in butyl rubber vulcanizates—at least in the first stages, we may well suppose that every sulfur bonding with rubber is initially of a polysulfide type, that is, in the first step of the reaction. Agreeing with this, we find that the temperature dependence of the initial rate of polysulfide formation gives an activation energy the same as that of the rate constant for sulfur decrease. Thus, the maximum of polysulfide formation is the result of two opposing reactions. We have one reaction in the course of which polysulfide is formed and which is coupled with the decrease of sulfur, and another process which leads to the destruction of the polysulfide. The height of the maximum would then be dependent upon the ratio between the rates of these two reactions. To the extent that these become commensurable, it must decrease, and high content of polysulfide should indicate that the destroying reaction is much slower than the decrease of sulfur.

It can be seen that the situation bears considerable resemblance to a reaction that proceeds through an intermediate product. Yet the state of affairs is considerably more complex than in most of the well-recognized examples of this kind, so we wish for the present to confine ourselves to a qualitative discussion. If, for instance, we think of the sulfur as the reactant, the polysulfide as the intermediate product and the vulcanizate (crosslinks) as the end product, then the increase in crosslinking should follow along an S-shaped curve. This is not always observed. Furthermore under these conditions, the crosslinking should never reach its end value while the polysulfide content is still decreasing. But examples of this are shown in Figure 12 with several reaction curves for *cis*-1,4 polybutadiene. Finally, a reasonably good agreement was found between the half-life times of sulfur decrease and the crosslinking (reciprocal equilibrium swelling) for the vulcanization of natural rubber with sulfur in the

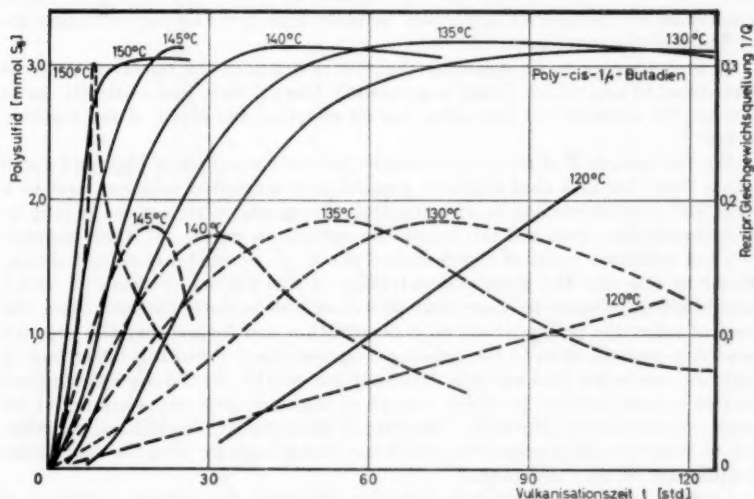


FIG. 12.—Increase in the reciprocal equilibrium swelling (Respr. Gleichgewichtsquellung) (solid curves) and change in polysulfide combined sulfur (broken curves) with the reaction time at various temperatures (*cis*-1,4 polybutadiene).

presence of zinc oxide. This shows that both these characteristics follow the same time law. This indicates that the crosslinking is rather tied in with the sulfur decrease which is connected with polysulfide formation. So the vulcanizate already contains the polysulfide which we considered to function as an intermediate product cannot be looked upon as the end product via the polysulfide. Evidently the polysulfide bound sulfur is an intermediate material with regard to an end product, which was not measured in this work, but which will be identical with the intramolecular heterocyclic ring systems which arise from the primary polysulfide bound sulfur. Numerous investigations by Moore, Bateman, Glazebrook, Ross, Porter, Saville and others²⁸, make this probable. A complete kinetic account would have to consider that the decrease of sulfur concentration proceeds autocatalytically and possibly the polysulfide itself is the catalyst.

According to preliminary evaluation of the curves in Figure 11, we find that the polysulfide formation can be very nicely expressed by the equation:

$$y = ax^b \cdot e^{-cx}$$

in which y is the polysulfide content of the vulcanizate, x is the reaction time, a , b , and c are constants, of which a is a function of initial concentration of sulfur. Good straight lines are obtained if we rectify the equation by determination of b and then plotting the experimental data according to:

$$\log \frac{y}{x^b} = \log a - c \cdot x \cdot \log e$$

It is now necessary to give an explanation of the shape of the curves for sulfur decrease, especially for those initially concave to the time axis. In this connection we may recall that sulfur decrease is an autocatalytic process, which is indicated by the lack of agreement between time law and concentration dependence of the rate ($n_c > n_d$).

It first appears to be desirable that we re-examine the question which is often debated and which Craig² has recently treated fully and critically, as to whether the solubility of the sulfur has an effect on the shape of the reaction curves.

We can assume that the initial concave form of the curves of Figures 4 and 8 results from the fact that sulfur is present in a saturated solution, and as a result will react according to an autocatalytic process of zero order as long as its concentration does not fall below the saturation value. If that happens then the inflection point of the S-shaped curve ($T = \text{constant}$) should always appear at one and the same concentration of free sulfur. Studies of *cis*-1,4 polybutadiene, Figure 8, show that this does not happen; for one thing the point of inflection is dependent on concentration and for another the concave curvature persists, even to the lowest concentrations. From this latter fact, it might be concluded that sulfur is decidedly less soluble in *cis*-1,4 polybutadiene than in natural rubber, in which convex or normal curve types are noted for lower concentrations, Figure 3. Because of the comparable chemical constitution of these two elastomers, we would not like to assume that the solubilities of sulfur are so very different.

Craig² emphasized the fact that we can eliminate the concave curvature of the reaction curves by merely adding small amounts of material, particularly of accelerators. That can be very easily explained by assuming that these compounds bring the sulfur into solution and that the polysulfides which form in the course of the reaction could act in this way to assist the "going into solution" of the sulfur: this is in line with Bergem²⁴, who thinks that every bound sulfur atom facilitates the further reaction of the sulfur with rubber. So if natural rubber contains certain but small amounts of impurities which are not removable by extraction, such as degradation products of proteins, then the solubility of sulfur may be increased. However, it is conceivable that the concentration of impurities is not sufficient to bring about complete solution at the higher concentrations of sulfur, so then the S-shaped reaction curves appear. If that is the case, it may be inferred that *cis*-1,4 polybutadiene is a very pure elastomer, since for it only the S-shaped reaction curves for sulfur decrease are found. Then perfectly pure natural rubber should also show only S-shaped reaction curves, and sulfur should be only moderately soluble in it, but this is not in agreement with the determinations of solubility of sulfur in rubber²⁵.

Another explanation would be as follows: We think of the concave shape of the reaction curves as indicating an autocatalysis which is also expressed by the lack of agreement between the time law and concentration-dependence of the rate, and which—since it can be ascribed only to reaction products—is brought about by polysulfide. That can be accepted because the maxima in polysulfide formation always coincide pretty well with the inflection points of the S-shaped reaction curves, and in any case the polysulfide content generally drops off whenever the rate of sulfur decrease begins to gradually diminish after the initial increase. Now it is entirely possible that impurities of the kind previously described can suppress the autocatalytic effect at low sulfur concentrations for the concentration of polysulfide is still very low; and that this is

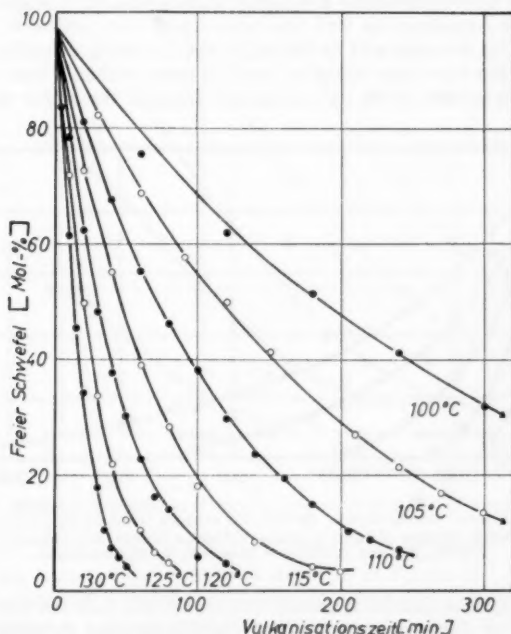


Fig. 13.—Concentration decrease of sulfur in Perbunan at various temperatures in the presence of DPG [(S₂)₂ and (DPG)₂ = 10 mmole/100 g compound].

no longer the case at high sulfur concentrations, when the polysulfide concentration has correspondingly increased. In other words, the appearance of either the one or the other type of curve would be a question of the ratio of concentrations of the impurities versus the polysulfide. But even if this supposition holds, we have no indication that the solubility limit of sulfur was ever reached. This concept is also inconsistent with determinations of the solubility of sulfur in rubber.

Se we see that it is difficult to interpret the shape of the reaction curves (sulfur decrease with time), but that based on all other observations on the decrease of sulfur concentration in 1,5 polyenes, it is evident that the process is

of the first order with respect to concentration. And after all, it appears much more likely to be a pseudo-monomolecular reaction than that the homolytic breaking of the S_8 ring is the rate-determining step. A detailed discussion of all the questions associated herewith has been given by Bateman, Moore and Porter²⁶.

B. THE INDIRECT, ACCELERATED VULCANIZATION OF RUBBER WITH SULFUR²⁷

The kinetics of the decrease of sulfur in accelerated vulcanizations of natural rubber has been studied much less in the past than it has been for unaccelerated vulcanizations. Ideas have been expressed on the matter, however, as attempts were made to understand the action of accelerators. Farmer¹ has devoted a whole chapter in his previously mentioned monograph on vulcanization to this question as he considered as well the concepts of other authors. Chiefly the kinetics of sulfur decrease will be treated in the following: it will be shown that the results which have been obtained make it seem probable that intermediate compounds are formed which we can assume transfer the sulfur to the rubber.

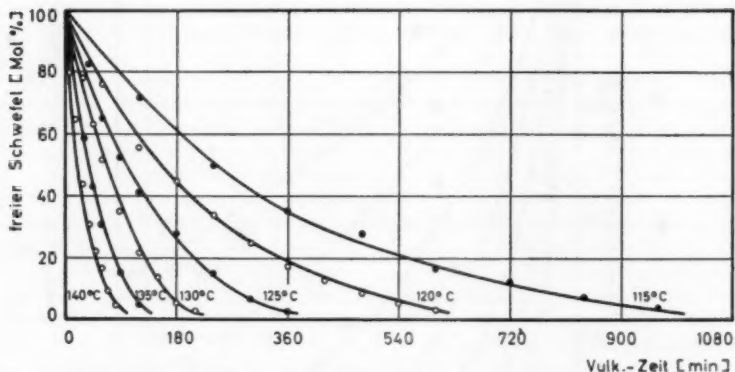


Fig. 14.—Concentration decrease of sulfur in natural rubber at various temperatures in the presence of MBTS; $(S_8)_0$ and $(MBTS)_0 = 10$ mmoles in 100 g compound.

Before going into details, it should be pointed out that the concave type of curves for sulfur decrease are not often found in indirect vulcanizations, even at high initial sulfur concentrations. However, there are exceptions, and concave curves appear initially confined generally to rather narrow reaction ranges. It is not easy to explain them directly, but they are responsible for the occasional induction period which appears in the crosslinking.

This has been repeatedly mentioned by Craig who has frequently discussed its appearance².

By way of illustration, Figures 13 and 14 show the decrease in sulfur for NBR and natural rubber when DPG or (MBTS) were used as accelerators at different temperatures. $[(S_8)_0$ and $(DPG)_0$ were each 10 mmoles/100 g of compound]. All the curves are convex to the time axis. The reaction curves have this form throughout when these accelerators are present.

Curves with initial concave curvature are found for the greater part of the sulfur concentration range when zinc diethyl dithiocarbamate (ZnDEDC) is

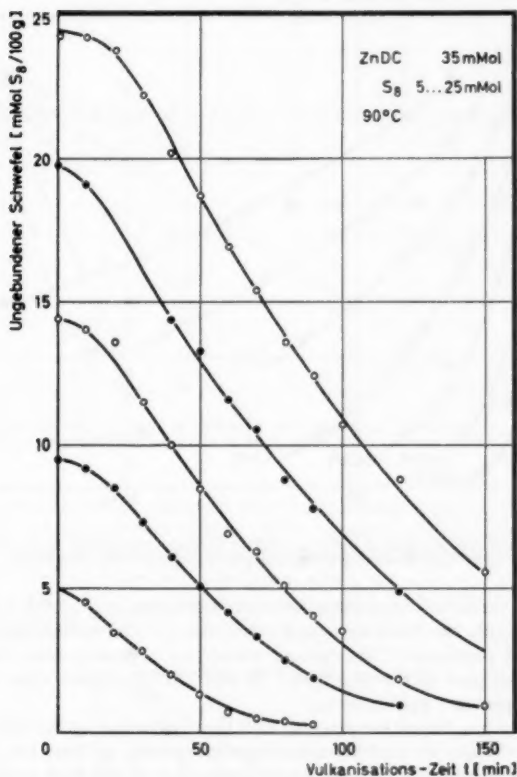


FIG. 15.—Concentration decrease of sulfur in natural rubber at 90°C and various initial concentrations, in the presence of ZnEDDC. Ungebundener = unbound.

the accelerator with natural rubber as is shown in Figure 15. Possibly there exists here a correlation between the type of curve and accelerator behavior. Its concentration in this vulcanization drops along a curve of similar nature. It is well, however, to notice that the ranges of the concave curvature in the curves show no trend with the concentration.

When an accelerator, such as *N*-cyclohexylbenzothiazolyl sulfenamide (CBS) is present, we note that the curves for sulfur decrease are initially concave. It is known that sulfenamides are accelerators whose use is accompanied by an induction period in the crosslinking and also in the decrease in sulfur. The curves of Figures 16 and 17 were obtained when $(S_8)_0$ and $(CBS)_0$, each = 10 mmole in 100 g compound, were used in vulcanizations of either natural rubber or NBR. Clearly defined induction periods are shown only for natural rubber, Figure 17. In the case of NBR, which probably could not be sufficiently well purified, they are always essentially shorter and tend to degenerate into concave curve forms, the appearance of which in this case is quite understandable.

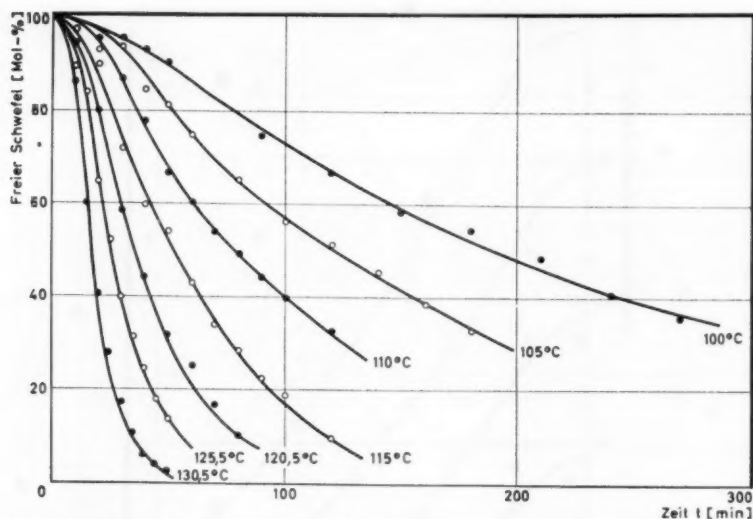


FIG. 16.—Concentration decrease of sulfur in NBR at various temperatures, in the presence of CBS (initial concentration of the reactants 10 mmoles in 100 g compound).

Inasmuch as curves for sulfur decrease were obtained of the type shown in Figures 15 to 17, we have confined ourselves to the evaluation of only the convex-curved portions of the curves, which, as is plainly seen, constitute by far the greatest part of the reaction. It will soon be shown that it is entirely justifiable to proceed in this way.

1. *The time law for sulfur decrease and the dependence of the rate constants on temperature.*—When we plot the experimental results, as they are found for an accelerated vulcanization, according to a time law of the first order, curves are

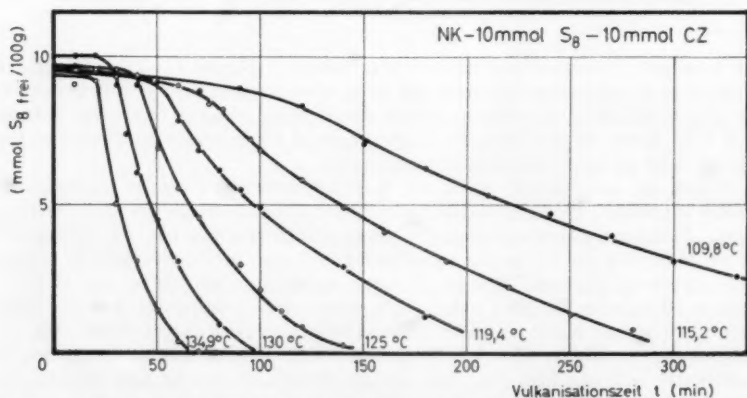


FIG. 17.—Concentration decrease of sulfur in natural rubber at various temperatures in the presence of CBS (initial concentration of reactants, 10 mmoles/100 g compound). CZ = CBS.

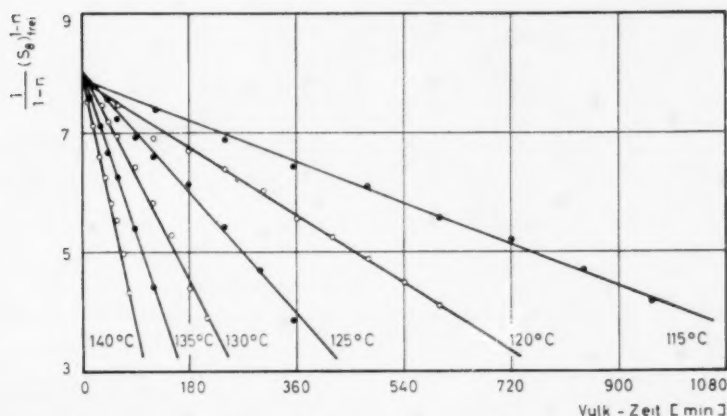


Fig. 18.—Concentration decrease of sulfur in natural rubber at various temperatures, in the presence of MBTS (10 mmole/100 g) according to the time law with $n_t = 0.8$. $[(S_0)_0 = 10 \text{ mmole/100 g compound}]$

usually obtained for sulfur decrease which are concave to the time axis over practically the whole reaction range. This means that the decrease of sulfur concentration must be a reaction of a fractional order, with $n_t < 1$. Judging from a great number of measurements taken where the most varied accelerators were used ZnMBT (Zn benzothiazolyl mercaptide), MBTS, organic bases, particularly DPG, ZnDEDC, and CBS we can decide that n_t for accelerated

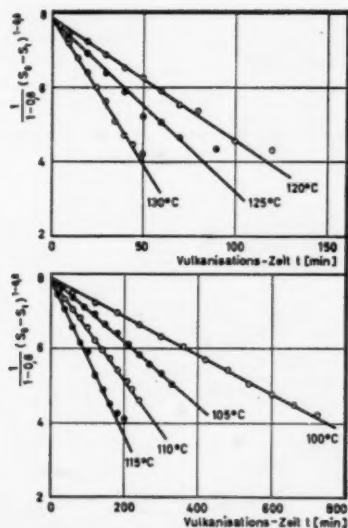


Fig. 19.—Concentration decrease of sulfur in NBR at various temperatures, in the presence of DPG (10 mmole/100 g) according to a time law with $n_t = 0.8$. $[(S_0)_0 = 10 \text{ mmole/100 g compound}]$.

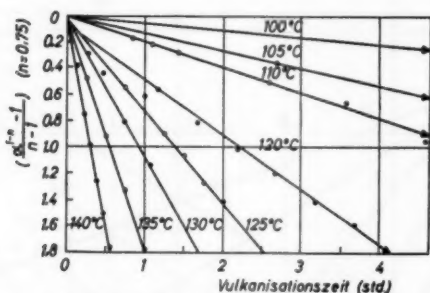


Fig. 20.—Concentration decrease of sulfur in natural rubber at various temperatures, in the presence of DPG, according to a time law with $n_t = 0.75$.

vulcanizations assumes values lying between 0.5 and 0.8. Results obtained up to the present show that the following systems are exceptions: sulfur/MBT/ZnO/Zn Stearate, sulfur/ZnDEDC and excess DPG as well as sulfur/MBTS when the accelerator is in molar excess. In these cases the sulfur-decrease reaction follows the first order law.

This may be demonstrated by several examples. Figures 18 and 19 show the decrease of sulfur concentration according to Equation 5 with $n_t = 0.8$ for the vulcanization of natural rubber in the presence of MBTS and of NBR in the presence of DPG, at various temperatures. The sulfur (S_0) and the accelerator were each at a concentration of 10 mmoles in 100 g of compound in each case. In Figure 20 is given a plot of the experimental data according to Equation 7; in this case, natural rubber was vulcanized at different temperatures, with 10 mmoles S_0 and 10 mmoles DPG for each 100 g of rubber compound. The value of 0.75 was found here for n_t . Finally, Figure 21 gives the decrease of sulfur according to Equation 5 with $n_t = 0.8$ for the vulcanization of Perbunan in the presence of CBS (sulfur and accelerator were each at 10 mmoles/100 g compound). The curves do not intersect the ordinate at the

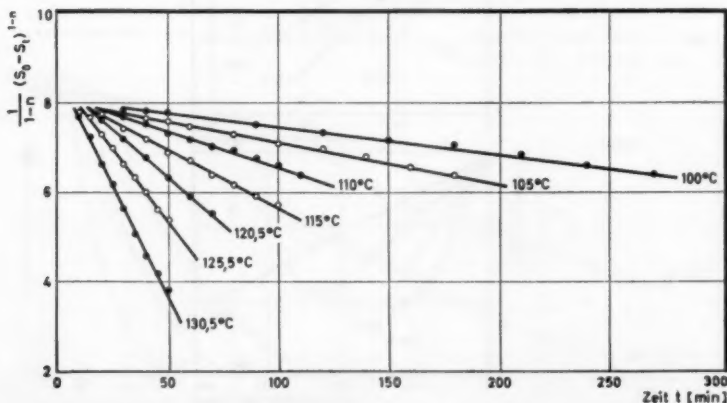


Fig. 21.—Concentration decrease of sulfur in NBR at various temperatures, in the presence of CBS (10 mmoles/100 g) according to a time law with $n_t = 0.8$. [$(S_0)_0 = 10$ mmoles/100 g compound].

TABLE V
RATE CONSTANTS OF SULFUR DECREASE, k_s^a FOR THE VULCANIZATION OF NATURAL RUBBER OR NBR IN THE PRESENCE OF VARIOUS ACCELERATORS (10 MMOL S₈ AND 10 MMOL ACCELERATOR IN 100 g COMPOUND)

Temperature		° C									
1	° K		Pale crepe, sulfur ^a $k_s^{0.5} \times 10^3$	Pale crepe, sulfur, MBTS $k_s^{0.5} \times 10^3$	Pale crepe, sulfur, DFG $k_s^{0.75} \times 10^3$	Pale crepe, sulfur, DFG, 150 mmol S ₈ ZnO/100 g $k_s^{0.5} \times 10^3$	Pale crepe, sulfur, CBS $k_s^{0.7} \times 10^3$	Pale crepe, sulfur, MBT, cyclohexyl amine $k_s^{0.45} \times 10^3$	NBR, sulfur, DFG $k_s^{0.5} \times 10^3$	NBR, sulfur, CBS $k_s^{0.5} \times 10^3$	NBR, sulfur, CA MBT $k_s^{0.5} \times 10^3$
0.00268		100			1.53				5.2	6.0	10.2
0.002645		105			3.19		8.28	11.82	8.6	10.5	
0.002613		109.8				5.60			13.77	17.0	16.0
0.002612		110			5.63	9.62	14.5		21.5	25.0	
0.002578		115		3.74							
0.002575		115.26									
0.002572		115.6									
0.002548		119.4						30.19			
0.002547		119.6				14.60					
0.002545		120.0		6.69	13.3				33.5	43.0	40.3
0.002542		120.5							52.0	79.0	
0.002512		125		11.1	20.8	23.35					
0.00251		125.5									
0.002512		125.00									
0.002482		130		17.5	31.0		41.3	49.92	80.0		
0.00248		130.3				39.40					
0.002478		130.5					53.6	83.55			
0.002452		134.9					99.65	123.4			
0.00245		135		27.6	52.9						
0.002448		135.6				55.80					
0.002422		139.6									
0.00242		140.0									
0.002418		140.6									
0.002392		145	5.5	45.5	96.0						
0.002362		150	9.7			87.0					
0.002342		153.8	17.5								
0.002308		160	24.5								
			35.1								
										102.0	98.0

^a In these series, the initial concentration of sulfur was 12.5 mmol/100 g.

initial value, which is to be traced to the induction period induced by sulphenamides. All the graphic representations, which are typical of many others, show that straight lines are obtained with sufficient accuracy, so that we can find confirmation of the values of n_t which have been determined. *In summation we can say that agreement exists with respect to the time law of sulfur decrease between direct and indirect crosslinking of rubber by sulfur, since $n_t < 1$ is the rule.*

Systems of curves like those shown in Figures 18 to 21 were plotted for a series of accelerated vulcanizations in which the concentrations of both the sulfur (S_8) and accelerator were 10 mmoles/100 g compound. Natural rubber and NBR were the elastomers. The rate constants were calculated from the slopes of the curves. These constants, because of the uniformity of concentration of the reactants, and in spite of the somewhat varying orders of reaction,

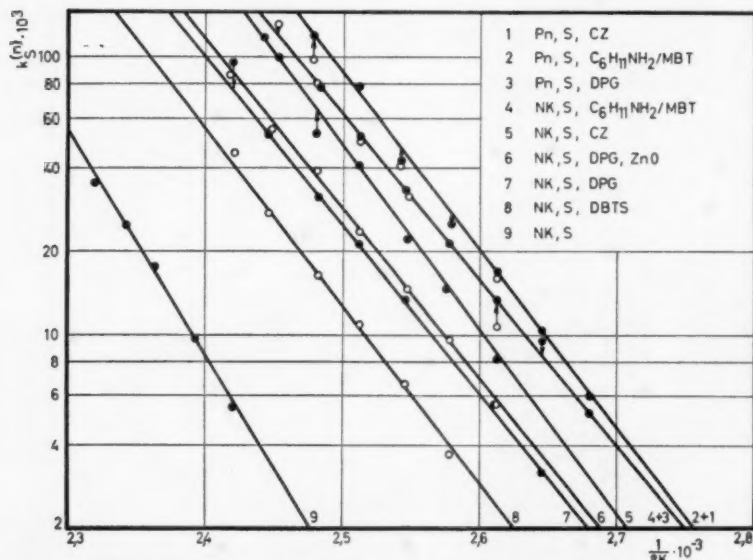


Fig. 22.—Temperature dependence of the rate constant for sulfur decrease in various systems of accelerated vulcanizations with equimolar additions of sulfur and accelerator. Pn = Perbunan (NBR), NK = natural rubber, CZ = CBS, DBTS = MBTS.

make possible an estimation of the approximate increases in rate which are, at times, brought about by the accelerator. They are brought together in Table V. For purposes of comparison, we have also included the rate constants of direct vulcanization of natural rubber with sulfur according to experimental Series 1 (see Section III, A).

The dependence of the rate constant on temperature according to Equation 11 is shown in Figure 22. It can be seen that the slope of Line 9 (natural rubber and sulfur) is somewhat steeper than for the others. The activation energy, calculated for instance by Equation 12, is actually appreciably lower for accelerated vulcanizations than for direct vulcanization with sulfur. According to previous determinations, the values run from 28 to 30 kcal/mole.

The maximum difference between the rate constants is considerable, and amounts to about 1.5 powers of ten ($T = \text{const}$). It will be noticed that MBTS (Curve 8) effects the smallest increase in rate; that it make practically no difference if the vulcanization of natural rubber in the presence of DPG made with or without zinc oxide (Curves 6 and 7); that sulfur in the presence of DPG reacts considerably faster in NBR than in natural rubber (Curves 7, 8 and 9); and in the vulcanization of NBR practically the same rate constants are observed for the decrease in sulfur (Curves 1 and 2), in the presence of CBS or an equimolecular mixture of MBT and cyclohexyl amine.

2. *The concentration dependence of the rate of sulfur decrease.*—It was explained in Section III, B-1 that n_t regularly has values between 0.5 and 0.8 for accelerated vulcanization; and in a given system, n_t was always independent of the temperature. It must now be emphasized that the exponent of the time law is generally also independent of the initial concentration of the reactants (sulfur

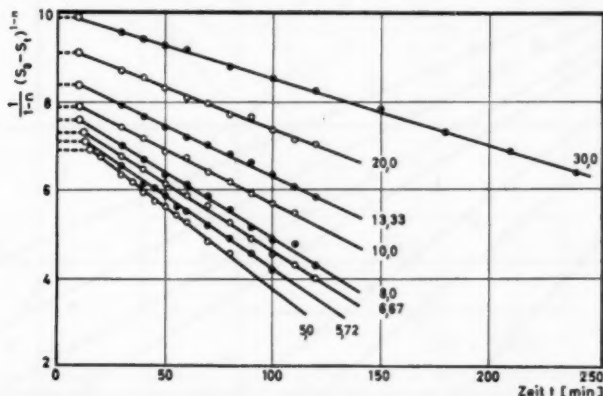


Fig. 23.—Concentration decrease of sulfur at 115° C in NBR in the presence of CBS fenamide (10 mmole/100 g) according to a time law with $n_t = 0.8$, at various initial concentrations of S_0 (5.0 to 30 mmole/100 g compound).

or accelerator) in accelerated vulcanizations. However, the rate itself is dependent on the molar ratio in which the two reactants occur. These facts show remarkable relations, which are of fundamental importance in explaining the nature of accelerated vulcanization, and which therefore shall be thoroughly set forth.

Figures 23 and 24 show the decrease in sulfur concentration according to Equation 5, with $n_t = 0.8$ for vulcanizations of NBR with increasing initial concentration of sulfur in the presence of CBS (Figure 23) and DPG (Figure 24) as accelerators. ($T = 115^\circ$ or 130° C; accelerator concentration is constant = 10 mmole in 100 g of compound).

The linearity of all the curves in these figures shows that n_t is independent of the sulfur concentration. But it is also shown that the slope of the curves and hence the rate constants in both cases decrease with the initial concentration of the sulfur. This indicates that also for accelerated vulcanizations there exists a lack of agreement between the time law and the dependence of the rate on concentration, for if this were not the case, then the straight lines would

have to be parallel. But what is shown in Figures 23 and 24 happens more often for accelerated vulcanizations. When we hold the initial concentration of sulfur constant ($T = \text{const}$) and increase that of the accelerator stepwise, we get experimental results like those shown in Figure 25 for the vulcanization of natural rubber in the presence of aniline. Here $T = 140^\circ \text{C}$ and the sulfur concentration was constant at 10 mmole S_8 in 100 g compound.

It can be seen that in such cases the slopes of the curves, and therewith the rate constants, at first increase with the concentration of accelerator, to finally become practically constant at higher concentrations, where the curves become nearly parallel. The fact that the rate constant for decrease of sulfur increases in spite of constant initial sulfur concentration is easily understood if we take into consideration the accelerating or catalytic action of the base. Yet it

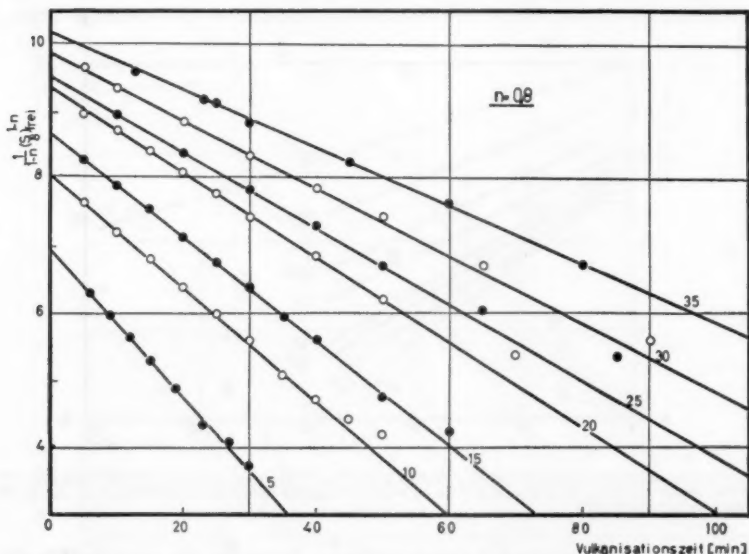


FIG. 24.—Concentration decrease of sulfur at 130°C in NBR in the presence of DPG (10 mmole/100 g) according to a time law with $n_s = 0.8$ at various initial concentrations of S_8 (5.0 to 35 mmole/100 g compound).

shows again that a lack of agreement between the time law and the dependence of rate on concentration, which is found, more or less clearly marked, in all accelerated vulcanizations, will exist also in this case. An exception to this is noted in the systems: sulfur/ZnMBT and sulfur/ZnDEDC, in which the rate of sulfur decrease is practically independent of the concentration of accelerator. This is possibly an indication that the solubility of the accelerators in rubber is rather limited, so that accordingly, their initial concentration is constant.

In view of this state of affairs, the dependence of the initial rate on the initial sulfur concentration is naturally of considerable interest. Understanding the essential relationships for complex reactions, such as accelerated vulcanizations, has proved to be best defined in the beginning of the reaction. Since overall time laws are valid in the preceding cases, the exponents of which are practically

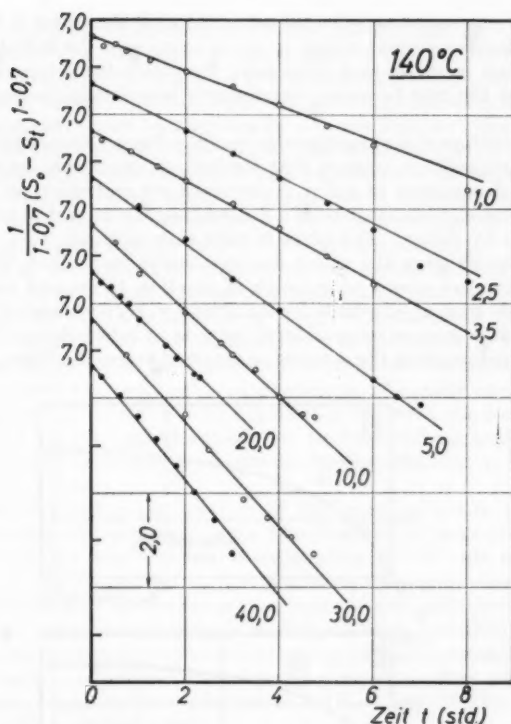


FIG. 25.—Concentration decrease of sulfur in natural rubber at 140°C in the presence of increasing amounts of aniline and at constant initial sulfur concentration (10 mmol S_0 in 100 g) according to a time law with $n_s = 0.7$.

independent of concentration, we can calculate initial rates according to Equation 13, with the help of the rate constants k' which are dependent on initial concentration and which are derived from the slope of curves like those in Figures 23 to 25.

It then appears:

(1) With constant initial sulfur concentration, the initial rate of sulfur decrease increases with increasing accelerator content, rapidly at first and then more and more slowly, to become practically constant when the accelerator is present in large excess. The rate constant k' thus shows this same dependence on accelerator content, since $(S_0)_s$ is constant.

(2) At constant initial concentration of accelerator the initial rate of decrease of sulfur rises rapidly at the start with the initial sulfur concentration, and then slower and slower, and tends to become constant at higher concentrations. But at the same time, the rate constant for decrease of sulfur decreases with the initial concentration of sulfur; and it follows from this, that the initial rate shows less increase with the initial concentration of sulfur than the applicable time law requires.

The relationships may be demonstrated by Figure 26 the individual graphs of which show clearly the course of the curves described under (1) and (2) above. It does not matter whether the accelerator content is kept constant

as the sulfur concentration is increased (a, b) or if the sulfur is kept constant and the accelerator content varied (c, d), in every case the initial rate of sulfur decrease at first increases and, after going through a transition range in which the growth in the rate becomes progressively less, finally becomes practically constant.

3. *Interpretation of the experimental results.*—From the considerations in the preceding paragraphs it appears that the lack of agreement between the time law and the dependence of sulfur decrease on concentration as found for accelerated vulcanizations must be of a different sort from that observed in direct vulcanization by sulfur. For while in that case although $n_i < n_c$ was found to be true, nevertheless the sulfur decrease could be defined by a valid law of chemical kinetics over a wide range of reaction times and concentrations. This also holds true, at all events for the time law, for accelerated vulcanization which here however must be considered more as an interpolation formula which can serve for determining the conversion attained in specified time, as well as the

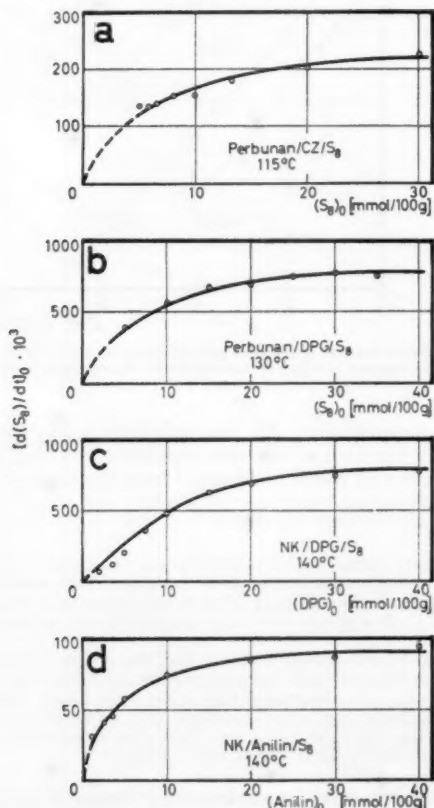


Fig. 26.—Relationship between initial rate of sulfur decrease and initial sulfur concentration (a and b) or accelerator content (c and d) in several indirect vulcanizations.

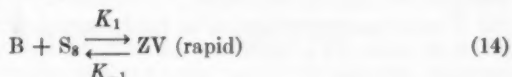
initial rate. The determination of the initial rate—as has been pointed out—would be more difficult and less accurate if done by the graphic method.

On the other hand, the dependence of rate on concentration, especially under the conditions of constant initial sulfur concentration and varying accelerator constant, in general cannot be described by a power time law, that is, it cannot generally be characterized by an order of reaction in the usual sense. Only when the relationships are observed under conditions of constant accelerator content and changing initial sulfur concentration is it sometimes possible to describe the results by a power law, yet we find—in contrast to the relations for unaccelerated vulcanization—that $n_c < n_t$ holds throughout. These kinetic characteristics of accelerated vulcanizations will certainly be observed, more or less pronounced in a great number of vulcanization processes.

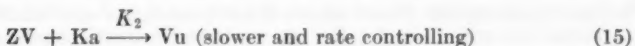
The dependence of the initial rate of sulfur decrease on the initial concentration of reactants (sulfur and accelerator) which is shown in Figure 26 has been observed frequently in the kinetics of catalysis by intermediate products, particularly in enzyme reactions²⁸. According to Michaelis and Menten²⁹ as well as Briggs and Haldane³⁰ we can explain the course of the curves with the assumption of a pre-established equilibrium between the *reactant*, the *catalyst*, and an *intermediate product*, which reacts further directly or indirectly to produce the end product.

Regardless of whether the reaction of the intermediate to yield the end product proceeds at the same rate as the establishment of the equilibrium or at a slower rate, we get identical formal expressions for the rate of decrease of concentration of the reactant; but it is clear that the equilibrium can only be really established if the reaction of the intermediate is the rate determining step.

If we apply these considerations to the relations frequently existing in accelerated vulcanization and assume that an equilibrium is actually established between reactant, catalyst and intermediate compound, then we will have in the first place, (when B = accelerator, ZV = intermediate compound, Ka = rubber, Vu = vulcanizate)



and



Then, following the explanation by Laidler²⁸, we can find an expression for the rate of formation of the end product or vulcanizate by computing the value of the concentration of the intermediate compound from the equilibrium as given by Equation 14, and introducing it into the expression for the rate of formation of Vu. Since the decrease in concentration of sulfur, which is of interest to us here and which is measured, corresponds to the reaction of the intermediate compound, we have:

$$-d(ZV)/dt = -d(S_8)/dt = k_2(ZV)(K_a) \quad (16)$$

Then from Equation 14 we get:

$$\frac{(ZV)}{(S_8)(B)} = K \quad (17)$$

and using $(S_s)_0$ and $(B)_0$ as the initial concentrations of sulfur and accelerator:

$$\frac{(ZV)}{[(S_s)_0 - (ZV)][(B)_0 - (ZV)]} = K \quad (18)$$

Equation 18 is quadratic in ZV, and hence it is usual and expedient to discuss the relationships for conditions when sulfur or accelerator is in excess.

We then have:

$$\frac{(ZV)}{(S_s)_0[(B)_0 - (ZV)]} = K \text{ for } (S_s)_0 \gg (B)_0 \quad (19)$$

and

$$\frac{(ZV)}{[(S_s)_0 - (ZV)](B)_0} = K \text{ for } (B)_0 \gg (S_s)_0 \quad (20)$$

Equations 19 and 20 which are now linear in ZV, gives for (ZV):

$$(ZV) = \frac{(B)_0(S_s)_0}{(S_s)_0 + 1/K} \text{ for } (S_s)_0 \gg (B)_0 \text{ and } (B)_0 = \text{const.} \quad (21)$$

$$(ZV) = \frac{(B)_0(S_s)_0}{(B)_0 + 1/K} \text{ for } (B)_0 \gg (S_s)_0 \text{ and } (S_s)_0 = \text{const.} \quad (22)$$

If we put the expressions for (ZV) from Equations 21 and 22 into Equation 16, we get for the decrease in concentration of the intermediate compound, and thus sulfur:

$$- [d(ZV)/dt]_0 = - [d(S_s)/dt]_0 = \frac{k_2(B)_0(S_s)_0(Ka)}{(S_s)_0 + 1/K} \quad (23)$$

and

$$- [d(ZV)/dt]_0 = - [d(S_s)/dt]_0 = \frac{k_2(B)_0(S_s)_0(Ka)}{(B)_0 + 1/K} \quad (24)$$

The dependence of the initial rate of sulfur decrease on concentration described by Equations 23 and 24, on the one hand, in Equation 23 with respect to initial concentration of sulfur at constant accelerator content, and, on the other hand in Equation 24 with respect to accelerator concentration at constant sulfur concentration, will of course be substantially determined by the relative magnitude of the two terms in the denominator.

The greater the value of K and hence the smaller $1/K$, the sooner can $1/K$ be neglected in comparison with $(S_s)_0$, for example, in Equation 23 in the case of increasing sulfur concentration, so that the $(S_s)_0$ term cancels and the initial rate becomes constant. Likewise, when in Equation 24 $1/K$ becomes negligible compared to $(B)_0$ and $(B)_0$ cancels, the initial rate becomes independent of the accelerator concentration and thus becomes constant. On the other hand, if the initial concentrations of sulfur or of accelerator in Equations 23 or 24 become very small, so that they may be finally neglected compared with $1/K$, then the initial rate of sulfur decrease must rise linearly either with the sulfur concentration (when accelerator is constant), or with the accelerator concentration (when sulfur is constant). Naturally, there are transition cases between these extremes. We know that the general shape of the curves to be expected corre-

sponds to what has been repeatedly observed by us for accelerated vulcanizations. (See Section III.)

It must be admitted that the description of the results by Equations 23 and 24 has, for the present, only a formal character. If we take as an example vulcanization accelerated with organic bases we must say: if, according to the ideas of Krebs²¹, we assume that bases react with sulfur to produce compounds with betaine-like structures which contain the sulfur in chainlike fashion which increase its reactivity, and that these compounds can form as intermediate compounds during vulcanization, we must nevertheless consider the fact that at present no details are known about the existence of a true equilibrium between sulfur, base and amine polysulfide under the conditions found during vulcanization, just as we know nothing about stoichiometric relations for the reactions which are given schematically according to Equation 14. Finally, we are not sufficiently well informed about the role of side reactions which may quite possibly take place in these cases. However, there will be much in favor of the explanation we have developed of *accelerated vulcanization being catalysis by intermediate compounds*, if in the following we can show that very good agreement between theory and experiment is obtained by appropriate treatment of the data according to Equations 23 and 24. From this it seems to us that the fundamental idea upon which the deductions above are based may very well prove to be correct.

If we write the reciprocals of Equations 23 or 24, we have:

$$1/[d(S_8)/dt]_0 = \frac{1}{k_2 K (S_8)_0 (B)_0 (K_a)} + \frac{1}{k_2 (B)_0 (K_a)} \quad (25)$$

$$1/[d(S_8)/dt]_0 = \frac{1}{k_2 (S_8)_0 (B)_0 (K_a)} + \frac{1}{k_2 (S_8)_0 (K_a)} \quad (26)$$

Equation 25 signifies that the reciprocal of initial rate of sulfur decrease will be a linear function of the reciprocal of the initial sulfur concentration, if the accelerator content is held constant; likewise, according to Equation 26, it will be a linear function of the reciprocal of the initial accelerator content, when the sulfur content is held constant.

Another evaluation, which leads to the same result, is obtained when we write the following for Equations 23 and 24:

$$\frac{[d(S_8)/dt]_0}{K} + [d(S_8)/dt]_0 (S_8)_0 = k_2 (S_8)_0 (B)_0 (K_a),$$

$$\frac{[d(S_8)/dt]_0}{K} + [d(S_8)/dt]_0 (B)_0 = k_2 (S_8)_0 (B)_0 (K_a)$$

After rearrangement, we obtain:

$$\frac{[d(S_8)/dt]_0}{(S_8)_0} = k_2 K (B)_0 (K_a) - K [d(S_8)/dt]_0 \quad (27)$$

and

$$\frac{[d(S_8)/dt]_0}{(B)_0} = k_2 K (S_8)_0 (K_a) - K [d(S_8)/dt]_0 \quad (28)$$

TABLE VI

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NBR WITH SULFUR AND CYCLOHEXYLAMMONIUM SALT OF MBT AT 115°C (Accelerator concentration constant (10 mmoles); sulfur varied)

$(S_0)_s$, mmoles/100 g	$\frac{1}{(S_0)_s}$	$k' \cdot 10^3$ ($n = 0.8$)	$\frac{[d(S_0)/dt]_s}{= k' \cdot (S_0)^{0.8}}$	$\frac{1}{[d(S_0)/dt]_s}$	$\frac{[d(S_0)/dt]_s}{(S_0)_s} \cdot 10^3$
5	0.2	37.5	0.136	7.35	27.2
5.72	0.175	33.0	0.133	7.52	23.5
6.67	0.15	31.0	0.141	7.10	21.3
8.0	0.125	29.0	0.153	6.54	19.1
10.0	0.1	24.5	0.155	6.45	15.5
13.33	0.075	23.0	0.183	5.46	13.8
20.0	0.05	18.5	0.203	4.93	10.1
30	0.033	15.0	0.228	4.39	7.6

According to these equations, we will get straight lines, if the quotients of the initial rate of sulfur decrease over the initial sulfur concentration (with accelerator constant), or over the initial accelerator content (with sulfur constant), are plotted against the initial rate of sulfur decrease. The value of the equilibrium constant assumed from Equation 18 can be derived directly from the slope of these lines, yet it would be of little significance to undertake such evaluation, for there is little probability that any single definite equilibrium exists (see later). Yet we can compute the rate constants for Equations 23

TABLE VII

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NBR BY SULFUR WITH DPG AT 130°C (DPG constant at 10 mmoles; sulfur varied from 5.0 to 35.0 mmoles S_0)

S_0 , mmoles/100 g	$\frac{1}{(S_0)_s}$	$k' \cdot 10^3$ ($n = 0.8$)	$\frac{[d(S_0)/dt]_s \cdot 10^3}{= k' \cdot (S_0)^{0.8}}$	$\frac{1}{[d(S_0)/dt]_s}$	$\frac{[d(S_0)/dt]_s}{(S_0)_s} \cdot 10^3$
5	0.2000	109.6	397.2	2.52	79
10	0.1000	89.0	561.6	1.78	56
15	0.0666	77.2	673.7	1.48	45
20	0.0500	73.0	692.1	1.44	35
25	0.0400	56.7	744.6	1.34	30
30	0.0333	50.6	768.9	1.30	26
35	0.0286	43.5	747.7	1.34	21

TABLE VIII

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH DPG AT 140°C (Sulfur concentration constant; DPG varied)

$(S_0)_s$, mmoles/100 g	$(DPG)_s$, mmoles/100 g	$\frac{1}{DPG}$	$k' \cdot 10^3$ ($n = 0.7$)	$\frac{[d(S_0)/dt]_s}{= k' \cdot (S_0)^{0.7}}$	$\frac{1}{[d(S_0)/dt]_s}$
10	2.0	0.500	14.0	0.070	14.3
10	3.5	0.286	24.0	0.120	8.34
10	5.0	0.200	42.5	0.210	4.72
10	7.5	0.133	73.0	0.366	2.74
10	10.0	0.100	95.0	0.485	2.10
10	15.0	0.067	125	0.625	1.60
10	20.0	0.050	138	0.690	1.45
10	30.0	0.033	150	0.750	1.33
10	40.0	0.025	150	0.780	1.33

TABLE IX

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH DPG AT 115°C
(Sulfur constant at 10 mmoles S_8 ; accelerator varied)

$(S_8)_0$, mmoles/100 g	$(DPG)_0$, g	$\frac{1}{DPG}$	$k' \cdot 10^3$ ($n = 0.7$)	$\frac{[d(S_8)/dt]_0}{= k' \cdot (S_8)_0^{0.7}}$	$\frac{1}{[d(S_8)/dt]_0}$
10	0.5	2.0	1.75	0.00876	114
10	1.0	1.0	4.25	0.0213	46.9
10	1.5	0.667	6.75	0.0338	29.6
10	3.0	0.333	11.1	0.0556	18.0
10	4.0	0.25	12.0	0.0602	16.6
10	5.0	0.2	12.5	0.0626	15.98
10	6.0	0.1668	12.2	0.0612	16.38

and 24 from the intercepts on the ordinate, provided the rubber, sulfur, and accelerator concentrations are known and K has been ascertained from the slope.

In Tables VI to X, we show the concentration dependence of the rate of sulfur decrease for several accelerated vulcanizations which we have thus far carefully studied. Diphenyl guanidine, aniline and CBS were the accelerators, and NBR and natural rubber were the elastomers. It should be noted that in all cases the sulfur concentration is given in mmoles S_8 per 100 g/compound and time is in minutes.

Figures 27 and 28 show that when NBR is vulcanized under the condition of increasing initial sulfur concentration and constant accelerator content (CBS or DPG), or under the condition of constant initial sulfur concentration and increasing accelerator content, good straight lines are obtained when the experimental data are evaluated according to Equations 24 and 25, or 26 and 27.

The plots according to Equations 25 and 26, or 27 and 28 should not be overrated, yet from a mathematical viewpoint, we have similar relations as in the description of an adsorption process. There, for instance, the equation of Freundlich, which is a power law, has only the value of an interpolation expression, which represents accurately the middle and strongly curved portion of the adsorption isotherm, but cannot include the range of low pressures or concentrations where a linear dependence exists or the saturation region at high concentrations of the adsorptive material. Langmuir's equation, which, at any rate, is so formed that it takes into account the initial state as well as the final state, is more comprehensive. Equations 23 and 24 also have just

TABLE X

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH ANILINE AT 14°C
(Sulfur constant = 10 mmoles; accelerator varied)

Aniline, mmoles/100 g	$\frac{1}{\text{Aniline}} \frac{1}{\text{mmoles/100 g}}$	$k' \cdot 10^3$ ($n = 0.7$)	$\frac{[d(S_8)/dt]_0}{= k' \cdot (S_8)_0^{0.7}}$	$\frac{1}{[d(S_8)/dt]_0}$
1.0	1.0	6.2	0.031	32.3
2.5	0.40	8.2	0.041	24.4
3.5	0.286	9.1	0.0452	22.2
5.0	0.20	11.6	0.0582	17.2
10.0	0.10	14.9	0.0746	13.4
20.0	0.05	16.5	0.0826	12.1
30.0	0.0333	17.3	0.0866	11.55
40.0	0.025	19.0	0.0952	10.5

such a form for they are fractional functions, which is also true of Langmuir's, and the numerator contains a product and the denominator a sum. It is clear, according to this, that even where there is catalysis by intermediate products, the dependence of rate on concentration can sometimes be described by a power formula, but the experimental data also fit Equations 25 and 26. So we must put all the more stress on the demonstration of a constant rate at high concentrations of the variable reactant; this is easier to attain when the accelerator is in excess with the sulfur concentration held constant, than when the reverse is the case.

In complex reactions—and the accelerated vulcanization by sulfur must certainly be so regarded—we can derive a kinetics which reveals the true character of the reaction only from results of studies in a very restricted range of concentrations; and even in such cases, the dependence of the rate on concentration must provide the decisive criterion for the reaction. This is why it was discussed so fully in the preceding cases.

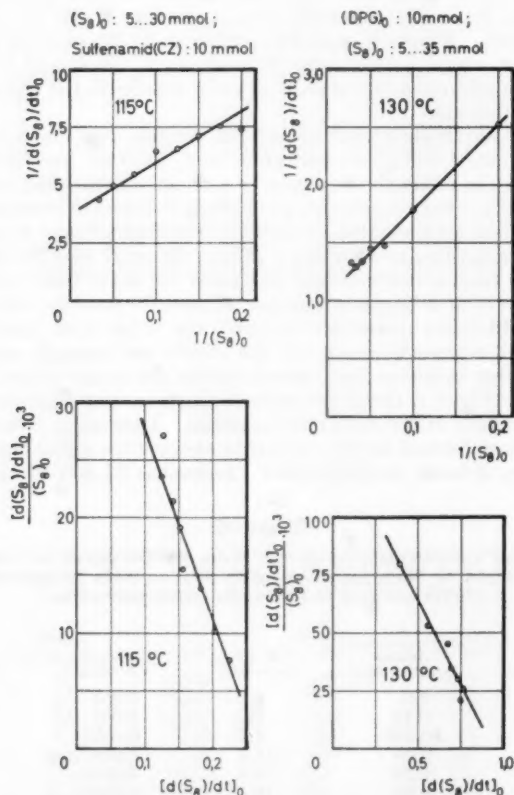


FIG. 27.—Dependence of the rate of sulfur decrease on concentration according to Equations (25) and (27) for several accelerated vulcanizations (experiments with NBR).

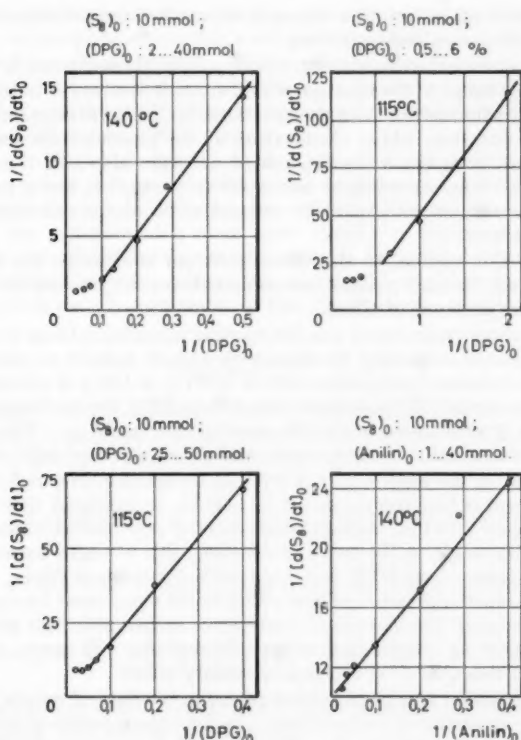


FIG. 28.—Dependence of the rate of sulfur decrease on concentration according to Equation (26) in several accelerated vulcanizations (experiments with natural rubber).

Nevertheless, we may at this time also investigate what should be expected with regard to the change of the sulfur concentration with time after the start. We get information about this, as Laidler²² has shown, when we integrate Equations 23 and 24. If we are dealing purely with an undisturbed catalysis by intermediate products, we should then expect from the resulting expression, (1) that the decrease of sulfur concentration, in the range of very low concentrations, would follow a time law of the first order, and (2) that exponents of the time law would be between $n = 1$ and $n = 0$ for medium sulfur concentrations, and (3) that a region of constant rate of sulfur decrease would be observed for very high sulfur concentrations (beginning of the reaction). To be sure, we should not expect complete consistency in what happens kinetically in this case with respect to the change of sulfur concentration with reaction time, because an effect on the rate of sulfur decrease by the reaction products (probably polysulfides which form in vulcanization) is not to be excluded. In other words, the autocatalytic nature of the sulfur decrease, as such, can obscure the relations. Nevertheless, one would have to observe that the exponent of the time law varies not only along a single reaction curve, but also with the initial

concentration of sulfur, in other words n_t for accelerated vulcanizations should show a dependence on concentration.

Yet the fact that the experiment, in every case, gives exponents for the time law over a wide range of the reaction which are independent of temperature and of the concentration relations of the reactants (sulfur or accelerator), brings us up against a situation, whose clarification at the present time seems scarcely possible. Only with the vulcanization of natural rubber in the presence of DPG and zinc oxide, according to our exploratory studies, was it probable that there was a variation with reactant concentration of the reaction order with respect to the time.

In closing this section, to the extent that our studies on the subject have been carried out, we may make a few comments on the kinetics of the decrease of sulfur in the presence of fillers.

Natural rubber (pale crepe) was the starting material in these investigations. All the compounds contained 10 mmoles S_8 and 10 mmoles accelerator (DPG or CAMBT (cyclohexylammonium salt of MBT)) in 100 g of compound. The inorganic filler Aerosil 165 and the carbon blacks CK3, Durex, Corax, Philbaack E and Vulcan 9 were added in various amounts (up to 60 g). The compounds also contained zinc oxide in many cases, and glycol was used with Aerosil.

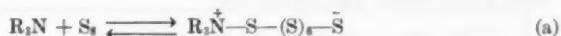
Particularly in the work with CAMBT as accelerator, in which the time law for sulfur decrease had the exponent $n_t = 0.45$, it appeared that neither the amount nor kind of added carbon black exerted any marked influence on the rate of sulfur decrease or the order of reaction; this was also basically true for the vulcanizations when DPG was used with the various fillers. It is noteworthy that even the presence of zinc oxide in the compound brought about no particular change in the kinetics of decrease of sulfur, although zinc oxide can affect the degree of crosslinking quite substantially. It seems that we can conclude from this that ZnO exerts a secondary effect.

A certain basis for this hypothesis is found in the data of several exploratory studies on the formation of polysulfides. In the vulcanization of natural rubber in the absence of zinc oxide, with aniline as accelerator, the polysulfide content of the vulcanizate was practically independent of the aniline concentration and of about the same magnitude as for direct vulcanizations by sulfur. If the aniline is replaced by CBS, the polysulfide content is found to be somewhat higher; but a two- to three-fold increase in the bound polysulfide fraction comes about first when zinc oxide is also present and its interference in the reactions appeared also in the formation of zinc sulfide. These are merely observations which mark out the area within which further quantitative research is to be done.

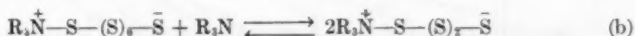
4. *The nature of the intermediate compounds which form in accelerated vulcanization.*—In the preceding section, it was shown that the kinetics of sulfur decrease in accelerated vulcanization leads to the conception, that there is a catalysis by intermediate compounds and the results of the cases treated heretofore are in relatively good agreement with the theory advanced by Michaelis and Menten²⁹ as well as Briggs and Haldane³⁰. Yet we must keep in mind that the equilibrium between sulfur, accelerator and intermediate compound as given in Equation 14 has only a formal character; for we know nothing about the stoichiometry of the reaction which is its basis, and—as will be explained later—we must reckon with the fact that we are dealing with several coexisting equilibria. Finally, of course, there is the possibility that side reactions take place, concerning which we can only conjecture.

In view of this state of affairs it is proper now to discuss ideas about the intermediate compounds which this work makes probable and which have also been proposed by other writers³¹. The nature of the intermediate products formed can still best be evaluated when organic bases are brought into the picture as accelerators, especially since in this case the results and indications of studies by Krebs³¹ can be drawn upon.

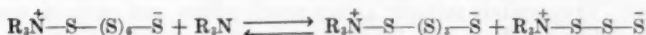
According to the explanations of that writer, we must suppose that the accelerating organic bases react with sulfur to form amine polysulfides with betain-like structures—not only by the vulcanization reaction but in other reactions of the sulfur—which react more rapidly to form the end product, since they contain the sulfur in chainlike form. In particular, an equilibrium will be established between sulfur, the amine and the corresponding amine polysulfide which we can formulate for the simplest case, as follows:



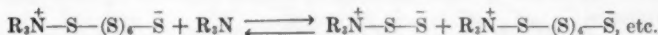
This equilibrium will not be the only one. It is especially likely that the sulfur content of the amine polysulfide will be less, if the amine is in excess; then the following equilibria are probable:



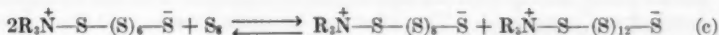
or



or



On the other hand, if sulfur is in excess, there is a possibility that amine polysulfides will form with higher sulfur content:

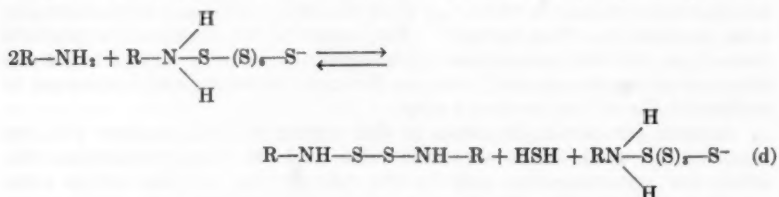


We know that with increasing content of base the concentration of kinetically active amine polysulfide molecules is considerably increased whereby compounds of high sulfur content are degraded to lower sulfur compounds. It is also evident that an excess of sulfur will not only bring about a shift in the equilibrium, but will also serve to increase the sulfur content of the already formed amine polysulfide molecules; that is to say that not all the excess sulfur acts to increase the number of active amine polysulfide molecules, which would shift the equilibrium in favor of the polysulfide, but rather sulfur will also be used by incorporation in the polysulfide chains of the already existing molecule.

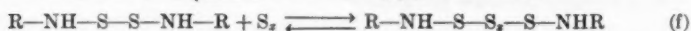
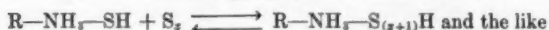
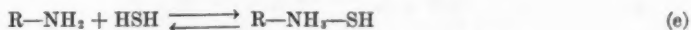
It seems, from the preceding, that we are dealing with several related equilibria, that is, composite equilibria. From this there may possibly be many a special inference with regard to the decrease of sulfur concentration with time.

The participation of hydrogen sulfide in connection with the vulcanization of rubber by sulfur is often discussed. It can be formed for instance, as Krebs³¹

has pointed out, by a direct reaction of sulfur with secondary or primary amines:



The hydrogen sulfide which appears in Reaction (d) will then combine with the amine to form an ammonium sulfide, which can go into equilibrium again with sulfur and an amine polysulfide; the disulfide which is formed will likewise form a polysulfide with sulfur, etc.



Using the example of the amine in the formulated reactions, which are not claimed to be complete, we can represent the formation of intermediate compounds. They contain sulfur in a very reactive form, and comprise a series of corresponding equilibria with the starting materials, sulfur and amine. Their existence can be shown to be probable by several qualitative, easily performed experiments.

If we add a small amount of elementary sulfur to a solution of triethanol amine (or diethanol amine, monoethanol amine, butyl amine, and the like) in a high boiling solvent like glycol (or paraffin oil or glycerine) and heat the mixture, we will notice that a dark red-colored zone forms around the undissolved sulfur, from which the sulfur goes into solution with the formation of a bottle-green compound. The color can be quite intense. If the material is cooled to room temperature, the intensity of the green color diminishes rapidly, and the solution finally becomes practically colorless. Reheating brings up the green color, and this disappears again on cooling. This cycle which, in our opinion, is the indication of a reversible reaction, can be repeated over and over again and may well be considered as an indication of the existence of an equilibrium, which is rapidly established between the amine, the sulfur and an amine polysulfide (as conceived by Krebs) and which is displaced in favor of the amine polysulfide by heating. Quite possibly the reaction of sulfur with rubber, in the case of acceleration by bases, has its start in this kind of equilibrium. At the present time, it is difficult to develop similar concepts about the activation of the sulfur in other accelerated vulcanizations, yet we call attention to the beginnings in which appear the various publications by Krebs³¹.

If the equilibria just discussed actually exist for a vulcanization accelerated with organic bases and if amine polysulfides are the real intermediate compounds which react with rubber in a rate determining step, then we can understand why the rate of decrease of sulfur depends on the strength of the base, as has often been emphasized; for it is clear that there will be a correlation between the ability of such amine polysulfides to react and the strength of the base.

Figure 29 shows the decrease in sulfur concentration for the vulcanization of natural rubber in the presence of a series of organic bases (equal molar content), at 140°C, as plotted according to Equation 7. Values of the exponent of the time law found here varied between 0.5 and 0.7.

Both tertiary bases, dimethylaniline and diethylaniline, have practically no effect on the rate of sulfur decrease; for Curves (1) and (2) essentially coincide with Curve (1a) which is for vulcanization without an accelerator. However, the two secondary amines, N-monomethyl aniline, Curve 3, and N-monoethyl aniline, Curve 4, both bring about a slight increase in the rate; in fact, the methyl compound is somewhat more effective than the ethyl, although we should have expected the opposite, according to the strengths of the bases. It is possible that there may be some steric hindrance in the case of the monoethyl aniline.

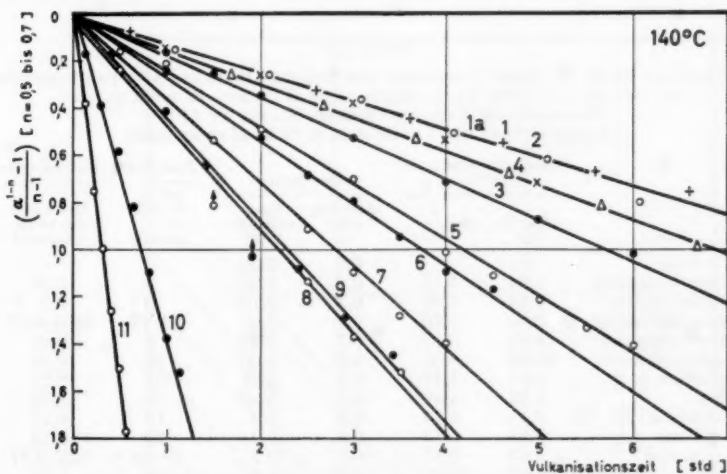


FIG. 29.—Decrease of sulfur concentration according to a time law with n_s about 0.7 at constant temperature and addition of equimolar amounts of bases and sulfur (10 mmoles/100 g) in natural rubber: S_0 alone (1a), N-dimethylaniline (1), N-diethylaniline (2), N-monomethylaniline (3), N-monoethylaniline (4), 1-naphthylamine (5), o-toluidine (6), aniline (7), m-toluidine (8), p-toluidine (9), benzylamine (10) and DPG (11).

The primary amines exert a very strong effect on the rate. It increases in the discernable sequence in Figure 29 for the amines here shown, and reaches the highest value which we observed for organic bases in the case of DPG, Curve 11.

This work confirms the fact that the acceleration of vulcanization by bases is tied in with the presence of active hydrogen attached to nitrogen, so the greatest increase in rate is gained with the primary bases. The color of the vulcanizate is also in agreement with this. The stronger the base accelerates, the more intense the color of the transparent vulcanizate (without zinc oxide). The color varies from a clear yellow for weak acceleration through orange to a dark red when the rate of decrease of sulfur is higher.

In Table XI are given, for various bases, the rate constants for decrease in sulfur calculated from the respective values of n_s which were found. Since

sulfur concentration was constant and the bases were used at equimolar concentrations, the values are quite comparable, and in general the exponents of the time law have values between 0.5 and 0.7.

If we plot the rate constants against the negative logarithms of the dissociation constants, K_b , of the bases we find a linear relation between these quantities for the primary amines used here, viz., 1-naphthylamine (Curve 5), *o*-toluidine (Curve 6), aniline (Curve 7), *m*-toluidine (Curve 8), *p*-toluidine (Curve 9) and benzylamine (Curve 10). Since DPG does not fit into this linear relationship we conclude that such a correlation is to be expected only with bases of comparable chemical structure. The studies confirm what has already been stated by Kratz and coworkers³⁴, namely that a parallelism exists between base strength and rate of sulfur decrease in accelerated vulcanizations; they also help to support the ideas developed above about the nature of the intermediate compounds which appear in accelerated vulcanization.

TABLE XI

CONNECTION BETWEEN RATE CONSTANTS FOR SULFUR DECREASE AND THE STRENGTH OF THE BASE IN THE VULCANIZATION OF NATURAL RUBBER IN THE PRESENCE OF VARIOUS ORGANIC BASES AT 140° C
(1 mole of base and 1 mole of S_8 in 10 kg of compound)

Base	Dissociation constant*, 25° C		Sulfur decrease		Bound base (limiting value)	
	$-\log K_b$ (pK)	$\log \frac{1}{K_b}$	Reaction order <i>n</i>	Rate constant $k \cdot 10^4$	$\frac{cs}{cs-100}$ mole %	Moles base per 10 kg. compound
Sulfur only	—	—	0.6	2.30	—	—
N-Dimethylaniline	8.94	5.16	0.2	2.02	3	0.03
N-Diethylaniline	7.44	6.66	0.3	2.13	0	0.0
Monomethylaniline	9.30	4.80	0.7	3.09	4-17	0.04-0.17
Monoethylaniline	8.89	5.21	0.7	2.43	3	0.03
1-Naphthylamine	10.08	4.02	0.5	4.00	43	0.43
<i>o</i> -Toluidine	9.61	4.49	0.7	4.87	21	0.21
Aniline	9.42	4.68	0.5	5.96	38	0.38
<i>m</i> -Toluidine	9.31	4.79	0.5	7.9	17	0.17
<i>p</i> -Toluidine	8.93	5.17	0.6	7.9	22	0.22
Benzylamine	4.63	9.47	0.7	22.2	27-62	0.27-0.47
DPG	3.89	10.21	0.75	53.9	54	0.54

* Derived from D'Ans-Lax, Taschenbuch für Chemiker und Physiker, Berlin, 1943, p. 845 and H. Staude, Phys.-Chem. Taschenbuch, Vol. II, Leipzig, 1949, p. 1616.

5. *Some special cases of indirect vulcanization by sulfur.*—It is quite possible that intermediate compounds always participate in indirect vulcanizations by sulfur yet this does not always appear so plainly in the kinetics of the decrease in sulfur concentration as in the cases previously discussed. This may be brought out in several examples.

a. Vulcanization in the presence of MBT and zinc oxide and ZnDEDC³⁵.—For vulcanization in the presence of MBT and zinc oxide, ZnMBT is the real accelerator, as we have pointed out. At first we found that the decrease in sulfur could be represented by a first order time law ($n_t = 1$), but a thorough checking and repeating of the experiments³⁶ showed that it obeyed better a time law with a fractional exponent ($n_t = 0.7$). The activation energy for the decrease in sulfur is in agreement with values for other accelerated vulcanizations, and was found to be 29.5 kcal/mole. The acceleration which is brought about by ZnMBT is relatively slight.

The MBT content in the rubber compound has no effect on the rate of decrease of sulfur. It is possible that ZnMBT is not completely soluble in rubber, so that a constant concentration of MBT is maintained. This can have as a consequence the lack of a dependence of the rate on the accelerator concentration.

Similar relations were found in vulcanizations accelerated with ZnDEDC. In this case, a decrease in sulfur was first found³⁷ which followed a zero order reaction, which agreed with measurements by van Alphen³⁷. Studies with a wider range of initial sulfur concentrations showed however that in this case too we must have a time law with fractional exponent, ($n_t < 1$). Actually the decrease in sulfur could be better described with $n_t = 0.6$. The accelerator content (ZnDEDC) in this vulcanization also had no effect on the rate of decrease of sulfur; and from a series of observations³⁸ we can deduce that the solubility of ZnDEDC in rubber is very low.

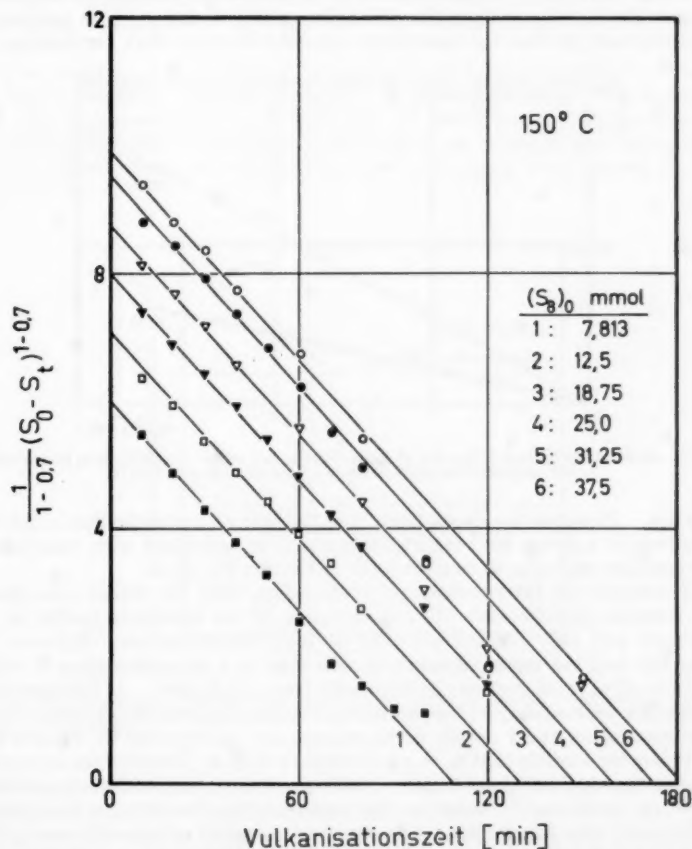


FIG. 30.—Decrease of sulfur concentration in natural rubber at 150° C and various initial concentrations according to a time law with $n_t = 0.7$, in the presence of a constant content of ZnMBT.

If we study the kinetics of sulfur decrease at constant temperature and increasing initial concentration of sulfur, we first find that n_i holds to its value, namely 0.7 (MBT) and 0.6 (ZnDEDC). In the case of acceleration by MBT, we get a family of straight lines when we plot the experimental data according to Equation 5 as is shown in Figure 30, and the slope is independent of the initial concentration, which means that the rate constant is independent of concentration, which was not the case for other accelerated vulcanizations. Hence there exists no lack of agreement between the time law and the dependence of the rate on concentration, that is $n_i = n_c$; and there exists proportionality between the initial rate and the initial concentration of sulfur raised to the 0.7 power, as is shown in Figure 31.

We could imagine that this result follows the fact that the rate is independent of MBT content; yet it is found that $n_i \neq n_c$ for vulcanizations accelerated with ZnDEDC, in which corresponding relations should be found. In other words, here the rate constant for the sulfur decrease falls with an increase the initial concentration of sulfur, as is the case in other accelerated vulcanizations, so that the rate shows a smaller increase than required by the

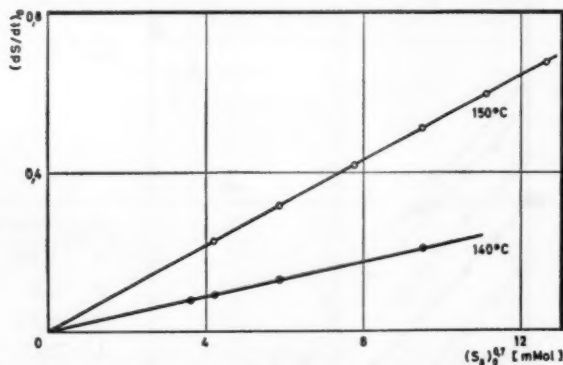


Fig. 31.—Relationship between initial rate of sulfur decrease and initial concentration in natural rubber at 140° and 150° C in the presence of a constant content of ZnMBT.

time law. However the dependence of initial rate on concentration is not well described by a power law; rather its course is in agreement with catalysis by intermediate products, as was set forth in Section III, B, 2.

If catalysis by intermediate products exists, then the initial rate should first increase linearly with the concentration of the reactants (sulfur or accelerator) and only become constant at high concentrations. Between the linear rise and the region of constant rate there is a transition stage in which the value of n_c must decrease continuously from one to zero. If this transition takes place over a fairly wide concentration range, then the dependence of rate on concentration under certain circumstances can be described by a power law, and it is quite possible that $n_c = n_i$ will then be found. Perhaps the agreement between time law and dependence of rate on concentration in the concentration range here considered for vulcanization accelerated by ZnMBT can be explained in this way, (see Figure 30). The range of constant rate is only reached at relatively high initial concentrations of sulfur. At present, we cannot tell if the explanation actually applies.

b. *The vulcanization of natural rubber in the presence of MBT, zinc oxide and zinc stearate*³⁹.—Vulcanizations in which thiazole "thiols" such as MBT or the corresponding disulfides are used show rather involved kinetics, but especially complicated relations are found when zinc stearate is also added; yet high quality vulcanizates are secured only under these conditions.

With MBT, zinc oxide and zinc stearate present, the decrease of sulfur concentration is distinguished by an induction period which shortens with rise in temperature; but after that period, it obeys a first order time law, independent of the vulcanization temperature as well as of the concentration of reactants. This result is in agreement with the findings of Bergem⁴⁰. An activation energy of about 19.5 kcal/mole is calculated from the temperature dependence of the rate constants according to Equation 12. This is in full agreement with statements of Gee and Morrell⁴¹, and is a considerably lower value than is usually found for accelerated vulcanizations. The difference in activation energy between the activated MBT vulcanization and the usual accelerated vulcanization is important and makes further detailed study advisable.

The presence of zinc stearate is accompanied by considerable increase in the rate of reaction. Because of the reduced activation energy, it is especially high at low temperatures; yet the difference in rate of sulfur decrease shown in ZnMBT-accelerated vulcanizations depending on whether zinc stearate is present or not, grows smaller and smaller with rising temperature, for the same reason.

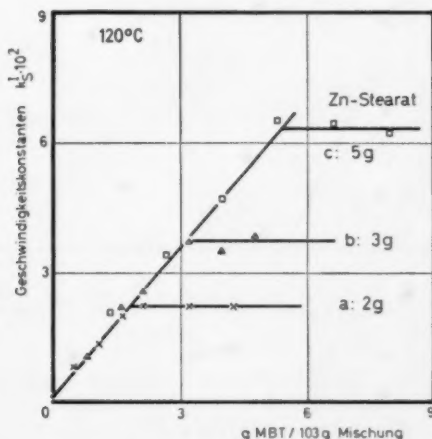


FIG. 32.—Dependence of the first order rate constant for sulfur decrease [(S₀) = const.] on the ZnMBT content, with the addition of various amounts of zinc stearate (experiments with natural rubber). Mischung = mixture.

Remarkable relations show up in the kinetics of the sulfur decrease when we hold the concentration of sulfur and the zinc oxide content constant (3.2 g and 4.07 g, respectively, in 103 g rubber compound) and increase the amount of added MBT stepwise, while we add a specific amount of zinc stearate, such as 2, 3 or 5 g, which we used in three series of experiments carried out at 120° C.

In the first place, it is found that even with such a wide variation in the concentration of the reactants, the time law follows a first order reaction ($n_t = 1$). But while the rate of sulfur decrease was independent of MBT content when zinc stearate was absent, we now find a pronounced dependence of the rate constants on accelerator content, which must be unconditionally ascribed to a mutual interaction between MBT and zinc stearate. If ZnMBT is actually only slightly soluble in rubber, it would seem that zinc stearate would increase its solubility.

If we plot the rate constants of sulfur decrease in these three series of experiments against the initial quantity of MBT, we get the relations which are shown in Figure 32. We see that the rate constant is a linear function of the MBT content of the mixture, that is, the dependence on concentration of the

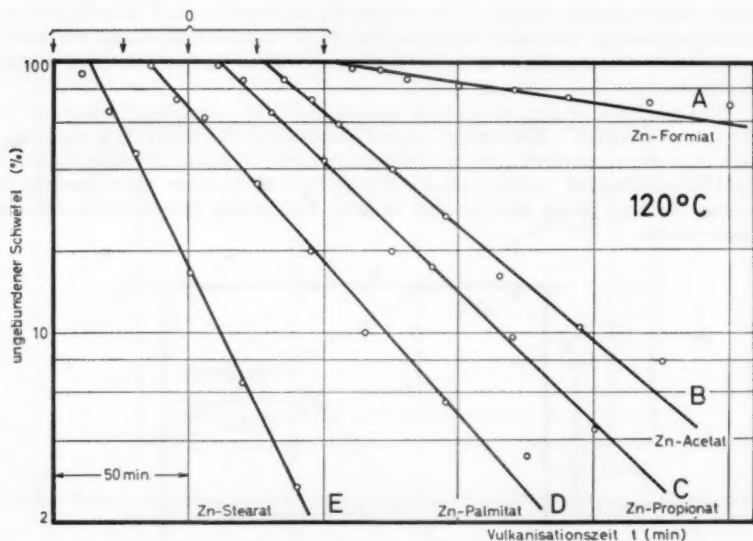


Fig. 33.—Concentration decrease of sulfur according to the first order, in natural rubber at 120°C with constant ZnMBT content or equimolar amounts of zinc formate, zinc acetate, zinc propionate, zinc palmitate, and zinc stearate.

rate of sulfur decrease (initial sulfur concentration constant) is a first order reaction with respect to accelerator. But we can also see that the range of concentration in which this linear dependence exists, itself depends on the zinc stearate content of the rubber compound. Evidently there is a critical concentration of MBT, beyond which the rate constant becomes independent of MBT content. It is a function of the zinc stearate content, and in all three experimental series, was reached when the molar ratio of MBT: zinc stearate was about 2:1; in other words, if we would keep the molar ratio of MBT and zinc stearate in a mixture at 2:1, and would successively increase the amount of this mixture, the first order rate constant of sulfur decrease would be a linear function of the amount of the mixture. From these studies we must infer, that the real accelerator again is an intermediate compound, formed from MBT, zinc stearate

and sulfur, and which would exert its maximum effect when and if ZnMBT (formed in situ) and zinc stearate are present in a 2:1 molar ratio, but at present, nothing is known about the nature of such a compound.

An analogous correlation is found between the rate of crosslinking measured by the reciprocal equilibrium swelling and the MBT content with constant zinc stearate although the dependence is nonlinear.

The fact that constancy of rate appears so suddenly and always at a well defined molar ratio of MBT and zinc stearate leads to the thought that ZnMBT and zinc stearate form a molecular compound. But we can also debate whether zinc stearate exists in the rubber in a micellar condition, which is characteristic of soaps, and the ZnMBT is involved in the formation of the micellar bonds.

In this connection, we may recall the fact which is perhaps known that the zinc salts of other fatty acids also increase the rate of decrease of sulfur. Figure 33 shows the decrease of sulfur to always following a first order path for equimolar additions of zinc formate, zinc acetate, zinc propionate, zinc plamitate and zinc stearate in a base recipe consisting of rubber, sulfur, MBT, and zinc oxide. Note that the curves are displaced from each other along the abscissa for the sake of clarity. It is to be seen that the rate constants for sulfur decrease (slope of the curves), increase with the length of the hydrocarbon chain in the fatty acid. We have not yet tried to find if the maximum increase in rate is attained every time with definite molar ratios of MBT and the zinc salt of the fatty acid.

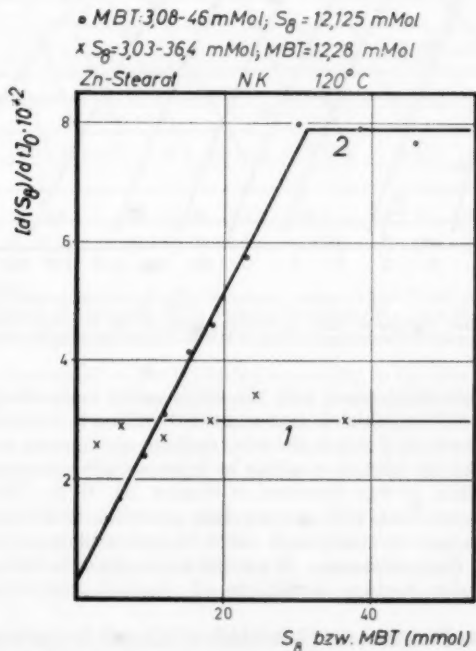


FIG. 34.—Relationship between initial rate of sulfur decrease and initial concentration of MBT (2) or S_0 (1) in the presence of a constant addition of zinc stearate (experiments with natural rubber).

If MBT, zinc oxide, and zinc stearate are kept constant in the rubber compound and the sulfur concentration is varied, the decrease of sulfur then follows a first order law in every case; yet the rate constant becomes a function of the initial sulfur concentration and drops monotonically with it. In particular, there is a linear dependence between the reciprocal initial concentration and the rate constant, which points to a concentration dependence of the rate of sulfur decrease which is of zero order with respect to sulfur. Actually we find that the initial rate of sulfur decrease is practically independent of the initial concentration of sulfur; as is shown by the crosses in Figure 34. This figure also shows the correlation between initial rate and MBT content with constant sulfur and stearate content, (shown by the points). The linear rise corresponds to that of the rate constant in Figure 32.

c. *The vulcanization of natural rubber by sulfur in the presence of MBTS.*—Dogadkin and coworkers⁴² have studied this and related reactions. Their fundamental hypothesis agrees with our results⁴³. According to it, MBTS

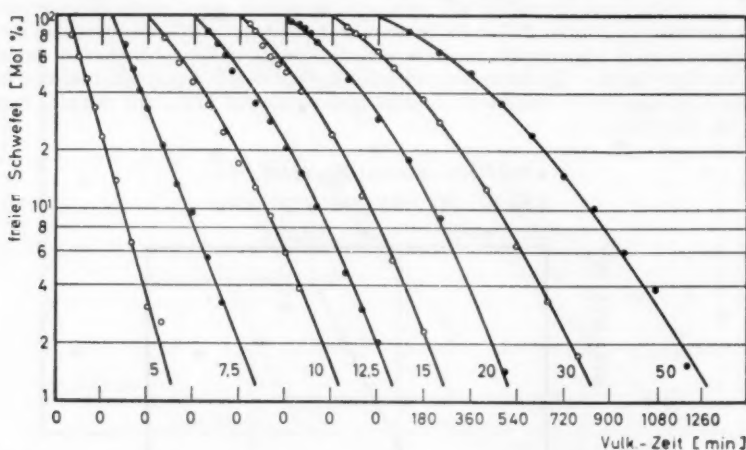


FIG. 35.—Concentration decrease of sulfur in natural rubber at 120°C [(S₀)₀ = 10 mmol in 100 g compound] in the presence of increasing amounts of MBTS in a plot according to a first order reaction.

splits into radicals which react with the cyclic sulfur molecules to form benzothiazolyl sulfur radicals, which in turn react with rubber to form the vulcanizate. There is some question, if this is the sole reaction; at any rate, such a theory is in agreement with the idea of catalysis by intermediate compounds for accelerated vulcanization, as was discussed in Section III, B, 3. However, peculiarities exist in connection with this reaction according to the studies as far as they have gone, and several details must be reviewed including decrease in concentration of the accelerator. It may be emphasized that this vulcanization was studied under various conditions of reactant concentration and of temperature.

First it is noted that the time law which is followed by the decrease of sulfur concentration, depends quite plainly upon molar relationships of the reactants, sulfur and MBTS. A change in the order of reaction with respect to time (n_t)

always takes place when the molar ratio of MBTS: S_8 becomes either greater or less than 1:1, that is, when we successively increase or decrease the accelerator concentration, keeping the sulfur content constant.

Figure 35 shows a group of reaction curves plotted according to the first order law for vulcanizations with constant MBTS content of 10 mmoles/100 g of compound and with increasing initial sulfur concentrations. As long as the sulfur concentration is less than 10 mmoles (MBTS in excess) we get straight lines, and the decrease of sulfur obeys a first order time law. When the sulfur concentration exceeds 10 mmoles (S_8 in excess), we get concave curves, that is $n_t < 1$. Actually, with these concentration ratios, the time law is satisfied by the exponent 0.8. If the sulfur concentration is held constant and that of MBTS is varied, we observe the same relations, as is shown in Figure 36. The value of n_t is again less than 1 as long as the concentration of MBTS is less than 10 mmoles/100 g compound. As soon as this value is exceeded, we get straight

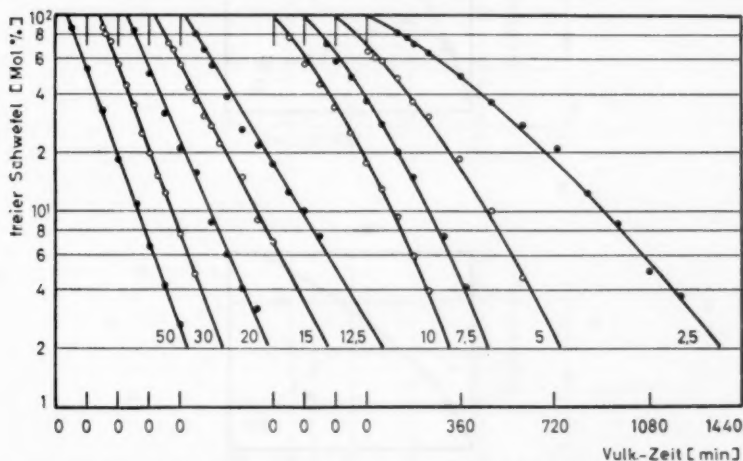


Fig. 36.—Concentration decrease of sulfur in natural rubber at 120°C with increasing initial concentration, in the presence of a constant MBTS content (10 mmoles/100 g), in a plot according to a first order reaction.

lines when the decrease of sulfur is plotted according to the first order. We see that the change in order comes suddenly, and is unmistakable in spite of the small difference ($n_t = 1$ or 0.8). The idea that this state of affairs is connected with a change in reaction mechanism is well founded, yet it was found that the activation energy for the decrease of sulfur remained unchanged at about 30 kcal/mole.

Now we should think that the change in reaction order with respect to time (n_t) makes no perceptible change in the dependence on concentration of the rate of decrease of sulfur because the initial rates calculated from the corresponding values of the rate constant and initial concentration are dimensionally similar.

If we examine first the relations when MBTS is constant and sulfur concentration is increased, we also find a lack of agreement between the time law and the dependence of rate on concentration. Yet a plot of initial rates against

initial sulfur concentrations still does not show if there is a catalysis by intermediate products, and the initial rates calculated from the first order constants do not fall on the curve, Figure 37b.

However, the dependence of the initial rate on MBTS concentration (constant sulfur content), as shown in Figure 37a, is in agreement with the existence of a catalysis by intermediate products, for we find that the increase in rate falls off sharply at high concentrations. But we find here also that the rates (broken line) calculated from the first order rate constants fall away from the curve. Yet we get straight lines in both cases if we plot the experimental data according to Equation 25 or 26 as is shown in Figure 38.

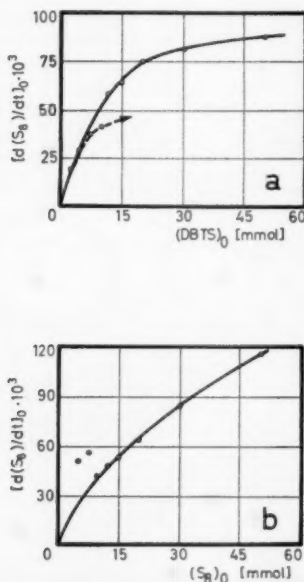


FIG. 37.—Relationship between initial rate of sulfur decrease and the concentration of MBTS, (a), or of S₈, (b), at 120° C (vulcanization of natural rubber). DBTS = MBTS.

We can say then the dependence on concentration of the initial rate of sulfur decrease, particularly under the conditions of constant sulfur and varying MBTS concentration can be considered in good accord with the existence of a catalysis by intermediate compounds, even though the sudden change in the order of the time law complicates the relations. Therefore, as far as fundamentals are concerned, the reaction mechanism proposed by Dogadkin and coworkers⁴², is supported since intermediate compounds were then assumed and formulated.

As has been mentioned, Dogadkin and coworkers⁴², assume that a radical splitting of MBTS—whether symmetrically or not may at first be ignored—is an essential reaction step in vulcanization accelerated with MBTS. Actually, Cutforth and Selwood⁴⁴ have shown that a homolytic splitting of the MBTS molecule is detectable at about 100° C.

Specific investigations⁴⁵ have shown that for the crosslinking induced by MBTS in NBR which contains vinyl side groups, the decrease in concentration of the disulfide actually follows a first order time law; and since the rate was found to be almost independent of the initial MBTS concentration the decomposition of MBTS seems very probably to be homolytic in this case.

We found more complicated relations in past experiences with the vulcanization of natural rubber accelerated with MBTS. The data may be summarized as follows:

1. The curves for decrease of MBTS concentration are S-shaped, and can be described by a time law with $n_t = 0.6$ along the portion which is convex to the time axis, and this does not depend on the temperature or the concentration ratio for the reactants (MBTS and S_8). The activation energy is about 23.3 kcal/mole.

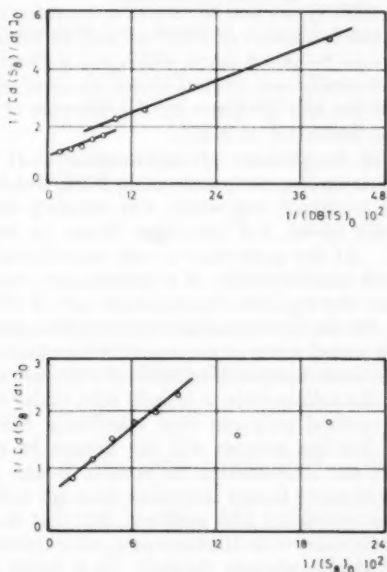


FIG. 38.—A plot of the data of Figures 37a and 37b according to Equations 24 and 25. DBTS = MBTS.

2. The rate of decomposition increases with the initial concentration of MBTS, and there is agreement between the time law and the concentration dependence of the rate; for when we plot the initial rates calculated from the rate constant and the corresponding initial concentration of MBTS against the square root of the initial MBTS concentration, we get a straight line through the origin, that is, $n_c \approx n_t$.

Thus in the example under consideration, MBTS reacted in no case according to the first order law; and hence we can surmise that sulfur possibly intervenes in the decomposition. However, if we study the decrease in concentration of MBTS at various initial concentrations of sulfur, we find:

3. The initial rate of decomposition of MBTS is entirely independent of the initial sulfur concentration, that is, the initial rate of decrease of MBTS is of zero order with respect to sulfur concentration.

Mercaptobenzothiazole is formed in considerable amount in the crosslinking of NBR induced by MBTS⁴⁵, yet not quantitatively as is the case in the reaction of diphenylmethane with MBTS⁴⁶. MBT also forms—practically independent of the temperature and MBTS concentration—to more than 60% in vulcanizations of natural rubber with sulfur, accelerated with MBTS. The occurrence of MBT should rest essentially on the reaction of MBTS with the hydrogen of the α -methylene group of the polymer chain. The resulting resonance-stabilized, polymer-chain radicals disappear either by combination (crosslinking) or react further in some other way, an idea which has also been advanced by Dogadkin and coworkers⁴².

Now while MBT is formed, at least over the greater part of the reaction range, according to a first order time law, when the crosslinking of NBR is induced by MBTS (in which process the rate constant is always a little lower than the decrease of MBTS), we find in case of a vulcanization of NR accelerated by MBTS that the formation of MBT as well as the decrease in MBTS concentration, follows an S-shaped curve which has a clearly-marked point of inflection. We have actually not made a closer study of such curves, yet we can be quite sure that the half-life times for the decrease of MBTS are always less than those for the formation of MBT.

*d. Vulcanization in the presence of sulfenamides*⁴⁷.—It has already been pointed out that in a series of experiments using NBR which had been exhaustively extracted with methanol, but which was certainly not absolutely pure, and to which CBS was added, the incubation times for sulfur decrease were comparatively small. At the same time it was established in this work that MBT is formed almost quantitatively in a preliminary, rapid reaction. From this it is inferred that the cyclohexylammonium salt of MBT is the real accelerator. Actually, the decrease in sulfur concentration went at the same rate but with no induction period when an amount of the ammonium salt equivalent to the sulfenamide was introduced at the start. In the case of CBS acceleration we may assume that the sulfenamide is rapidly split under the influence of the impurities and for practical purposes that essentially MBT and cyclohexylamine are present. Yet the process will not always be so simple. It was already mentioned in the introduction to Section B and also demonstrated that CBS shows a noticeably longer induction time for sulfur decrease in the case of natural rubber (extracted with acetone), but that the decrease of sulfur follows a curve which is concave to the time axis, after the end of the induction period, which is not always sharply defined. It is found that $n_i < 1$ holds again for this curve. The induction periods vary widely with the chemical structure of the sulfenamides, as is shown for several cases in Table XII. In agreement with data obtained by Feldshtein, Eltingon and Dogadkin⁴⁸, it is found that N,N-dicyclohexyl benzothiazolyl sulfenamide brings about a considerably longer induction time than the monocyclohexyl derivative (CBS); and since N,N-diisobutyl benzothiazolyl sulfenamide shows a much longer induction period than N-monoisobutyl benzothiazolyl sulfenamide, we may perhaps infer that sulfenamides with hydrogen on the nitrogen generally have shorter induction periods than the corresponding disubstituted derivatives.

There is no doubt that sulfenamides are subject to a radical dissociation, which has been repeatedly emphasized by Dogadkin and coworkers⁴⁸, and which is the starting point for their discussion of the accelerating action of the sulfenamides. The break down to radicals is manifest, according to the Russian workers, because many a sulfenamide can accelerate the thermal vulcanization

of synthetic rubbers, and we were able to fully confirm this⁹. Hence the dissociation kinetics of sulfenamides in organic solvents is particularly interesting. However, we have never yet succeeded in bringing the decomposition under control. The results of a number of exploratory studies led us to conclude that the cleavage of CBS takes place in a very short time, always, after a very long induction period is reproducible. According to the reaction curves this is without question an autocatalytic process. The sudden beginning of the reaction as well as its very rapid continuation make it understandable, why the

TABLE XII

INDUCTION PERIODS AT VARIOUS TEMPERATURES FOR VARIOUS SULFENAMIDES
(R₁ and R₂ are the groups attached to the amide nitrogen)
Induction period, min

A. Determined from reciprocal of equilibrium swelling

Benzothiazolyl sulfenamide, R ₁ , R ₂	110°	115°	120°	125°	130°	135°	140°	145°
R ₁ = cyclohexyl R ₂ = cyclohexyl	200	212	130	100	—	46	30	—
R ₁ = hydrogen R ₂ = isopropyl	144	101	75	51	33	25	15	—
R ₁ = isopropyl R ₂ = isopropyl	—	163	105	73	50	34	24	17
R ₁ = hydrogen R ₂ = cyclohexyl	—	—	37	26	20	13	9	6

(Thiazolinyl sulfenamide)

B. Determined from the decrease of sulfur

R ₁ = hydrogen R ₂ = cyclohexyl	70	51	40	32	25	18	—	—
R ₁ = cyclohexyl R ₂ = cyclohexyl	246	162	100	79	50	38	25	—
R ₁ = hydrogen R ₂ = isopropyl	103	80	53	40	25	19	13	—
R ₁ = isopropyl R ₂ = isopropyl	—	140	81	64	43	28	21	15
R ₁ = hydrogen R ₂ = cyclohexyl	The period here is too short for accurate measurement.							

(Thiazolinyl sulfenamide)

induction time of sulfur decrease during vulcanization is fairly sharply defined in many cases; for the accelerating system apparently forms very quickly. The dependence of the reciprocal equilibrium swelling on the reaction time also provides an important contribution to our understanding of the way in which sulfenamides work.

Figure 39 shows the sulfur decrease in the vulcanization of natural rubber in the presence of N,N-diisobutyl benzothiazolyl sulfenamide (DIBS) at various temperatures (sulfur concentration = 10 mmoles S₈; accelerator concentra-

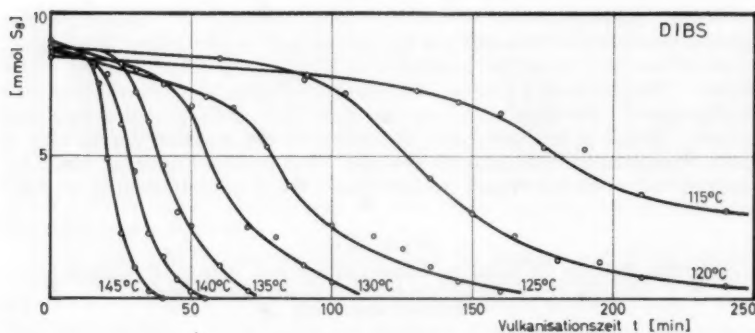


Fig. 39.—Concentration decrease of sulfur in natural rubber at various temperatures in the presence of diisobutyl benzothiasolyl sulfenamide (DIBS); concentration of reactants, 10 mmoles/100 g compound.

tion = 10 mmoles DIBS). Without discussing these curves in detail, we may point out that in this case, the induction period is very long and the end never clearly defined, so the reaction curves necessarily follow an S-shaped pattern. We should not be so much interested here in how we can define or determine an induction period in such cases, but we should consider, rather, the curves in Figure 40 corresponding to those in Figure 39 which show the dependence of the reciprocal equilibrium swelling on reaction time. It can be seen that for all temperatures a sharp increase in crosslinking starts suddenly and becomes steeper and steeper with increase in temperature. A very sharp maximum is

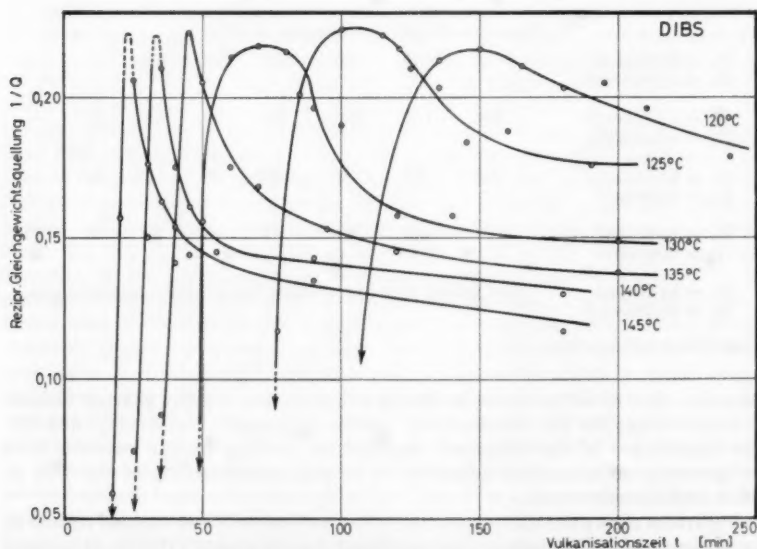


Fig. 40.—Increase of the reciprocal equilibrium swelling, $1/Q$, in the vulcanization of natural rubber at various temperatures, using sulfur (10 mmoles S_8) and DIBS (10 mmoles/100 g).

reached at higher temperatures, but this becomes progressively broader as the temperature is reduced; and in all cases, the crosslinking again falls off after the maximum is passed. The maxima occur somewhat close to the points of inflection shown in Figure 39, while the sudden rise in crosslinking sets in when the curves for sulfur decrease in Figure 39 assume a definite concave curvature. It is notable that the qualitative observations made above about the decomposition of CBS are also expressed in both Figures 39 and 40. Without doubt, this peculiar and still incompletely understood course of the reciprocal equilibrium swelling with reaction time is a consequence of the radical dissociation of the sulfenamide in which the rubber becomes involved during crosslinking. However, first of all, it is not clear why the crosslinking again decreases when the sulfur begins to react with increasing speed.

In this connection it is all the more surprising, that the kinetics of the sulfur decrease after the induction period, (during which, as we have seen, quite complicated reactions take place which evidently lead to the synthesis of the system which accelerates the decrease of sulfur) is just as accurately provided as in the case of other accelerated vulcanizations. In particular, we again find an activation energy of 28 to 30 kcal/mole, and this is to be sure *not in good agreement* with the observations of Dogadkin, Beliatkaya, Dobromyslova and Feldstein⁴⁸. They calculated an activation energy of 14 kcal/mole for the combination of sulfur with SBR in a vulcanization accelerated with N,N-diethylbenzothiazolyl sulfenamide. We consider this value much too low, but we readily agree that the evaluation of reaction curves is a difficult task, especially, as Dogadkin and coworkers mention, when the curves take on a marked S-shape. It may be pointed out in this connection, that even when long induction periods are brought about by sulfenamides, the dependence of rate on concentration, especially when sulfur concentration is constant and sulfenamide content is increasing, point again to a catalysis by intermediate compounds.

C. DIRECT VULCANIZATIONS

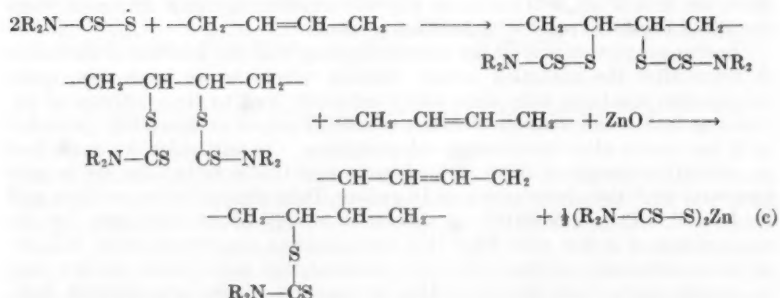
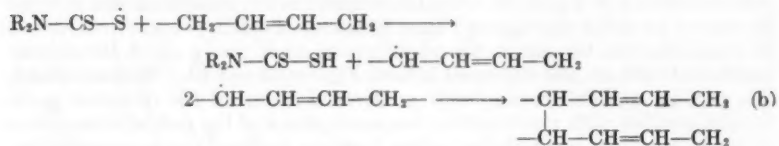
1. The vulcanization of 1,5-polyenes by compounds of the thiuram series.—

a. The direct thiuram vulcanization of natural and synthetic rubber⁵⁰.—In the following, "direct" thiuram vulcanization will be understood as the vulcanization of 1,5 polyenes using N,N'-tetrasubstituted thiuram disulfides (TD) or a mixture of the corresponding monosulfide (TM) and sulfur in the molar ratio TM:S = 1:1.

Such vulcanizations have been studied many times in the past from a technological as well as a chemical standpoint, chiefly because of the fact that on the one hand the thiuram disulfides as such bring about a vulcanization of 1,5 polyenes, yet on the other hand they act as accelerators of vulcanizations with sulfur. The crosslinking in every case is connected with the presence of zinc oxide. Craig and coworkers⁵¹, who have recently issued a series of valuable contributions to the explanation of thiuram vulcanizations, also reviewed the results published in preceding years on this subject⁵², and reference should be made thereto.

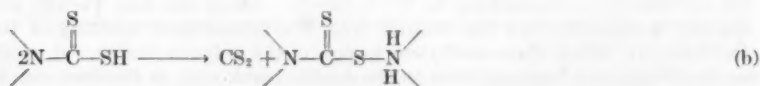
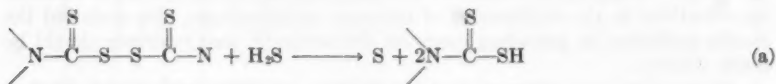
It has often been assumed that the thiuram disulfides bring about, more or less exclusively, a crosslinking by C—C bonds. Along this line, Farmer and Michael⁵³, proposed that the radicals from the symmetrical splitting of the disulfide, (a), attack the α -methylene groups of the polymer chains, (b), while Jarrijo⁵⁴ pictured their addition to the double bonds, (c), as the first step in

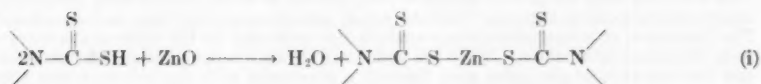
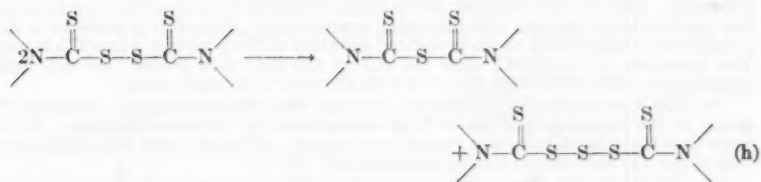
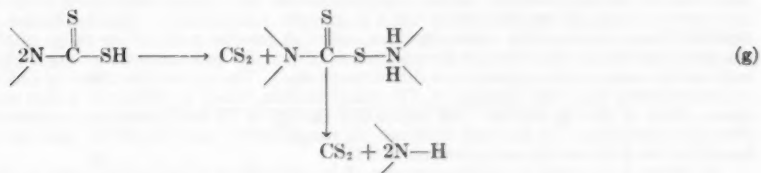
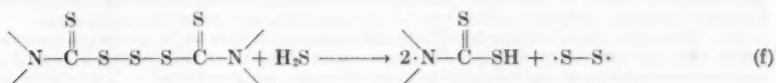
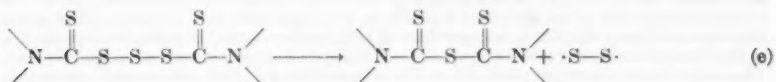
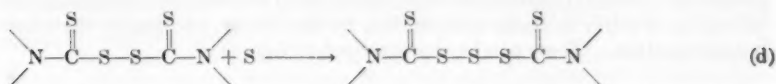
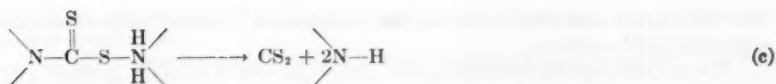
the reaction:



Today it is considered certain that crosslinking by C-C bridges, if it exists at all, is not the only type of crosslinking⁵⁴. However, the formation of sulfur crosslinks—as will be shown later—should not follow as simply as Bruni⁶, pictured. His idea was that thiuram disulfide is transformed into thiuram monosulfide with liberation of highly active sulfur which then effects the vulcanization.

Craig and coworkers⁵¹ discussed the mechanism of thiuram vulcanization very thoroughly, drawing on all known factual material concerning the chemical reactions of thiuram disulfides. According to that work, the process is initiated by hydrogen sulfide which is supposed to form in a side reaction. It reacts with thiuram disulfide to form dithiocarbamic acid and sulfur which then reacts with thiuram disulfide to form thiuram trisulfide. It is further assumed then that an equilibrium is established between thiuram disulfide, thiuram monosulfide and thiuram trisulfide; and the thiuram trisulfide is supposed to form dithiocarbamic acid and S₂ radicals in reacting with hydrogen sulfide or split out these radicals directly while forming thiuram monosulfide. The vulcanization would then be substantially effected through the S₂ radicals. Thus we would have to assume something like the following reactions by the thiuram disulfide under the conditions of a vulcanization:





After these preliminary observations, we may collect the results of kinetic studies and try to coordinate them with the ideas on the mechanism of thiuram vulcanization which have thus far been developed in organic chemistry.

The vulcanizates were thoroughly extracted with ethyl acetate in order to determine unreacted thiuram disulfide and any dithiocarbamate which formed. The extracts were collected in a volumetric flask and the dithiocarbamate in the solution was determined by distilling off the solvent, dissolving the residue in acetone, diluting with distilled water and titrating conductometrically at 40° C with hydrochloric acid. After back titration of most of the excess acid the mixture was finally titrated conductometrically with a solution of copper sulfate to determine the unreacted thiuram disulfide. The sulfur content of

the vulcanizate was determined by the combustion method⁴⁷ after thorough extraction with acetone.

We can distinguish kinetically four partial processes in pure thiuram vulcanization, namely: the decrease in concentration of the thiuram disulfide, the increase in zinc dithiocarbamate which forms in all thiuram vulcanizations, the taking up of sulfur in stable combination by the rubber, and finally the cross-linking reaction. These can be characterized as follows:

a. In vulcanization by thiuram disulfide (TD) in the presence of excess zinc oxide the concentration of TD falls and approaches zero under all conditions. Over the greatest range of the reaction the decrease in concentration of TD obeys a first-order time law and this behavior is independent of temperature and TD concentration as well as the zinc oxide content of the compound. These relations are found for all 1,5 polyenes. The same observations are made when TD is reacted in solution with model compounds such as, for example, geraniol or dihydromyrcene in the presence of zinc oxide, an activation energy of about 23 kcal/mole was calculated from the temperature dependence of the first order rate constant. This was an average value of numerous experiments.

b. Vulcanization of rubber by TD in the presence of zinc oxide is always accompanied by the formation of zinc dithiocarbamate (ZnDC) which brings about the outstanding stability of the vulcanizate in air at higher temperatures⁴⁸. Two-thirds of the thiuram disulfide which is introduced is converted in the vulcanization to ZnDC, regardless of the temperature, of the concentration of TD, of zinc oxide content or of any special chemical constitution of the 1,5 polyene under study. The formation of ZnDEDC also obeys a first order time law over the greatest part of the range of the reaction, and this is also true for the reaction of TD in the presence of zinc oxide with such model compounds as geraniol or dihydromyrcene. The rate of formation of ZnDC is always slower than the decrease in TD concentration, which is evident in a rate constant which is always smaller. An activation energy of 23 kcal/mole was calculated from the dependence of the rate constant on temperature, and this is the same as is found for the decrease in concentration of TD.

c. When a mixture of thiuram monosulfide and sulfur which corresponds to the composition of TD, is used, we again find that 66.6 mole per cent of zinc dithiocarbamate is formed. And yet the formation of the dithiocarbamate is characterized by an induction period which decreases with increasing temperature. From this it seems to us that a condition is established which is realized instantly or very rapidly when TD is used. The formation of ZnDEDC, after the end of the induction period, proceeds again according to a first order time law, and with the same activation energy.

d. The rate constants for thiuram decrease and dithiocarbamate formation decrease in the homologous series of N,N'-tetrasubstituted thiuram disulfides. At the same time the activation energy remains unchanged. In other words the special structure of the TD only affects the frequency factor.

e. The decrease in thiuram always runs faster than the dithiocarbamate formation. This indicates that the process proceeds through one or more intermediate compounds, among which could be thiuram trisulfide, which were proposed by Craig and coworkers⁴¹. The formation of intermediate compounds is also indicated by the color of the extracts from thiuram vulcanizates. They are yellow to brown, (depending on concentration), and the intensity of the color goes through a maximum with the vulcanization time. The extracts of fully reacted vulcanizates are nearly colorless; evidently the intermediate compounds are used up.

f. The rate constants for thiuram decrease and dithiocarbamate increase are dependent upon the zinc oxide content of the rubber compound. The rate constants, and therewith the rates, increase linearly with rising zinc oxide content at constant initial concentration of TD. If we choose some constant ratio of TD to zinc oxide and add this mixture in increasing amounts, we find that the rate constant for thiuram decrease remains practically unchanged, while that for dithiocarbamate formation again climbs linearly with the zinc oxide content. As far as the decrease in thiuram is concerned, it is seen that its rate under these conditions will be a linear function of TD concentration, that is, the dependence of the rate on concentration is a first order process. If we put a great excess of zinc oxide into the rubber and then increase the initial concentration of TD stepwise, the rate constant for ZnDEDC formation remains constant and that for thiuram decrease becomes a linear function of the reciprocal of the initial concentration of thiuram disulfide, which means that ZnDEDC formation is only

an indication of the change of zinc oxide content and the decrease in thiuram is then a process of zero order.

g. In the reaction of rubber with TD in the presence of zinc oxide, sulfur is taken up in stable combination with the rubber. The bound sulfur as a function of the vulcanization time goes through a poorly defined maximum which, independent of the temperature, is about 28 to 30% calculated on the amount of TD used. Completely reacted vulcanizates contain 25% sulfur, calculated on the TD introduced. This is in agreement with Dogadkin¹⁰.

h. The bound sulfur tends toward a limiting value of 33% before the maximum is reached. In this range of the reaction, the combination of sulfur with rubber follows a first order time law and the rate is the same as the decrease in concentration of TD. It is worthy of note that crosslinking is quite unappreciable while the chief part of the sulfur is combined. From this it can be seen that the stable combination of the sulfur does still not represent the real crosslinking reaction; and since the decrease in concentration of TD goes at the same rate as the chemical binding of sulfur, the decrease in thiuram also is not tied in with the crosslinking process. Figure 41 shows the temperature dependence of the rate constants for TD decrease and for sulfur pickup (they both fall on Line I) as well as for dithiocarbamate formation, Curve II.

i. In Figure 42, to secure an overall view, are brought together curves obtained at 100°, 110°, 120° and 130° C, for the decrease in thiuram, I, for dithiocarbamate formation, II, and for sulfur combination, III. It is seen that the points of intersection of the three curves form a spherical triangle, and that Curves I and II always intersect about where 25 to 30% of the thiuram disulfide is still present. It is also noticed that the sulfur content of the vulcanizate (calculated on the amount of TD introduced) is already practically constant, and in any case drops only a little (after the slight maximum is past). But the ZnDC is still far from its limiting value. All this, along with the fact that ZnDC formation does to a constant limiting value of two-thirds of the TD which

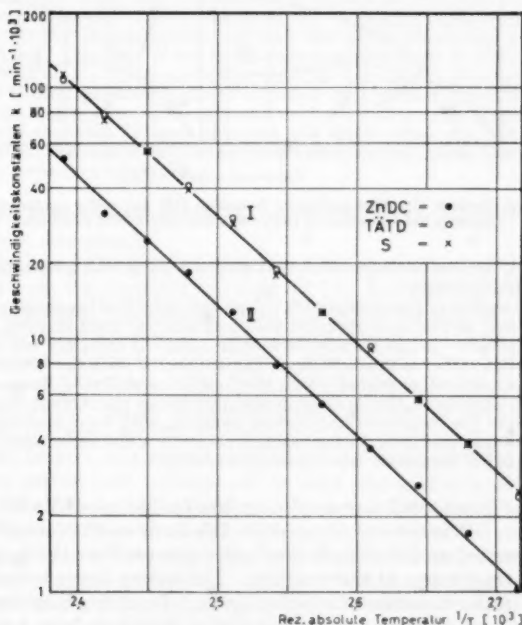


Fig. 41.—Temperature dependence of the first order rate constant for thiuram decrease and sulfur combination (I) as well as for dithiocarbamate formation (II) in the direct thiuram vulcanization of natural rubber (experiments with TETD(TATD)).

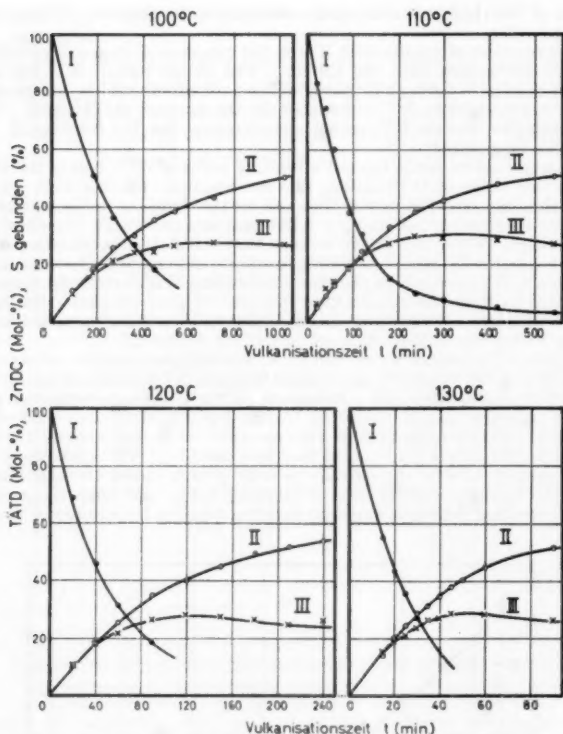


FIG. 42.—Thiuram decrease (I), dithiocarbamate formation (II) and sulfur combination (III) in direct thiuram vulcanizations at 100°, 110°, 120° and 130° C (TETD).

was introduced, inspires the impression that we are dealing with a stoichiometric process in thiuram vulcanizations.

j. Careful studies of the change with vulcanization time of the reciprocal equilibrium swelling (benzene) as well as of modulus values at different temperatures, show that the crosslinking reaction—as has already been mentioned—is certainly not tied to the decrease of TD, but rather is much more closely connected with the formation of ZnDC, even if it has an induction period which the formation of ZnDC does not show. According to past experience, the increase in modulus values at constant elongation as well as the increase in the reciprocal equilibrium swelling, with vulcanization time, can till now likewise be described over a large reaction range by a first order time law, and a rate equality with ZnDC formation has a great probability.

Craig² has interpreted our results on the formation of ZnDC as a second order reaction. It is natural to question this because the formation of ZnDC can be represented as following a first order process over the largest part but not over the total range of the reaction. Deviations occur toward the end of the reaction in the direction of a higher order. In such a case the question always comes up whether we are dealing with a deviation from a reaction order which applies to the greatest part of the range or if another order of reaction is to be specified which then must be valid for the total range. In this connection we may remark that the formation of ZnDC in experiments with model com-

pounds in solution is found to be a first order reaction over the whole range. Surely, for this reason, we can maintain for the present, that the decrease of TD and the formation of ZnDC are basically first order processes with respect to time with deviations therefrom near the end of the reaction.

k. The rate of the partial processes is affected not only by zinc oxide but also to a remarkable extent by finely divided silica, such as Aerosil. The rate increase which is brought about by silica, without changing the chemical reactions either qualitatively or quantitatively, is appreciably greater than with zinc oxide alone. The rate constants are linear functions of the amount of any particular Aerosil added. It is especially noteworthy, however, for the Aerosil materials, that they bring about a rate increase that is independent of their specific surface (sq. m/g). The relations are somewhat different in the case of precipitated silicas, for which no such clear connection between rate increase and surface area was found. This may indicate a more complicated fine structure for the particles⁶⁰. From all this it appears that thiuram vulcanization in the presence of silica follows the course of a heterogeneous catalysis. Perhaps we must generalize this statement since zinc oxide itself has a similar effect, even though it must be considered at the same time as a reactant. It is certain that direct thiuram vulcanization takes place at the surface of the zinc oxide particles, and for this reason we must assure a good dispersion of zinc oxide in a rubber compound if the vulcanizate is to be of the highest quality. The heterogeneous catalytic nature of thiuram vulcanization, especially in the presence of silica, is shown by the fact that its effectiveness for increasing the rate of the partial reactions can be eliminated by the addition of a sufficient amount of glycol. Evidently the glycol is preferentially adsorbed on the surface of the silica particles, and with an adequate concentration forms a monomolecular layer, which must lead to the elimination of the catalytic activity.

l. In discussing the chemistry of thiuram vulcanization it seems important to say that apparently, zinc oxide seems to display a specific activity, for according to experience, it cannot be replaced by any other oxide. The other metal oxides produce the corresponding metal dithiocarbamates, as does zinc oxide, when they are heated with thiuram disulfides. The yield of the metal-dithiocarbamate salt is rather high, namely about 90%, based on the thiuram disulfide used; and, except in the case of zinc oxide, this high yield of dithiocarbamate is also obtained when rubber is present, but in those cases, no crosslinking occurs. This is found only when zinc oxide is present, in which case, 66% of the available TD goes over into zinc dithiocarbamate. So we speak of a dithiocarbamate deficiency in thiuram vulcanization, which comes about through the simultaneously-occurring crosslinking.

It has already been indicated that thiuram vulcanization proceeds through an intermediate compound.

Along this line, we know that the sum of the amounts of sulfur as they can be calculated from the experimental data on TD, ZnDEDC, and bound sulfur, S_b , in the vulcanizate (all calculated on the sulfur content of the TD used) never comes up to 100 g-atom per cent. This was shown in particular in experiments with tetraethylthiuram disulfide⁶¹. Hence sulfur in soluble compounds must remain in the extracts. The dependence of this fraction of the sulfur, called "soluble sulfur" S_i , on the reaction time is shown in Figure 43. It can be seen that S_i increases rapidly at the start of the reaction, and goes through a maximum—to be sure, not apparent in all cases—at about 25%, and then decreases. The curved path corresponds to what was said in c. about the color intensity of the extracts. The maximum occurs about where Curves I and II intersect in Figure 41, and up to this time, furthermore, scarcely any crosslinking has taken place. There must be an extractable sulfur compound even in the completely reacted vulcanizate, which we have never yet been able to isolate or identify ($S_i \approx 8$ g-atom%). This S_i value is obtained from:

$$(S_i) = 100 - (TETD) - (ZnDEDC) - (S_b)$$

where the initial concentration of TETD = 100.

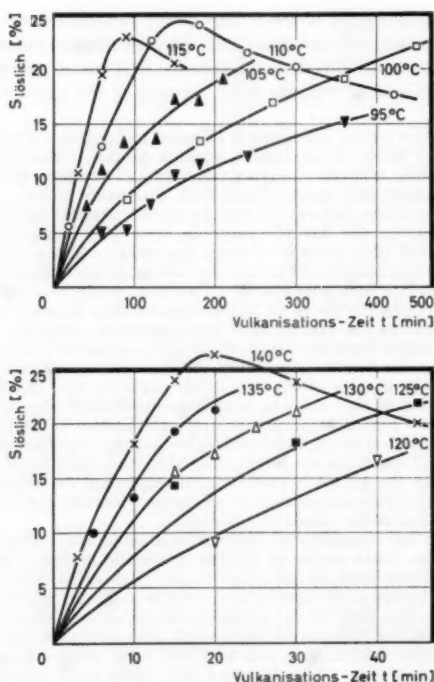


FIG. 43.—Dependence of the "soluble (löslich) sulfur" upon the reaction time at various temperatures in pure thiuram vulcanizations.

If we recall that the decrease in concentration of TD and the increase of bound sulfur are first order processes with equal rates at least over the greater part of the reaction range, and the bound sulfur approaches a limiting value of 33 g-atom percent (calculated on the initial amount of TETD), then the following must apply in the starting range of the reaction:

$$\frac{(S_0)}{100 - (TETD)} = \frac{2}{3} \quad (29)$$

$$\frac{(ZnDC) + (S_l)}{100 - (TETD)} = \frac{3}{3} \quad (30)$$

From the two equations we get:

$$\frac{(S_0)}{(ZnDEDC) + (S_l)} = \frac{1}{2} \quad (31)$$

and finally we have:

$$(S_0) = 33.3 - \frac{2}{3}(TETD) \quad (32)$$

$$(ZnDC) = 66.6 - \frac{2}{3}(TETD) - (S_l) \quad (33)$$

$$(S_2) = \frac{1}{2}(ZnDEDC) + (S_l) \quad (34)$$

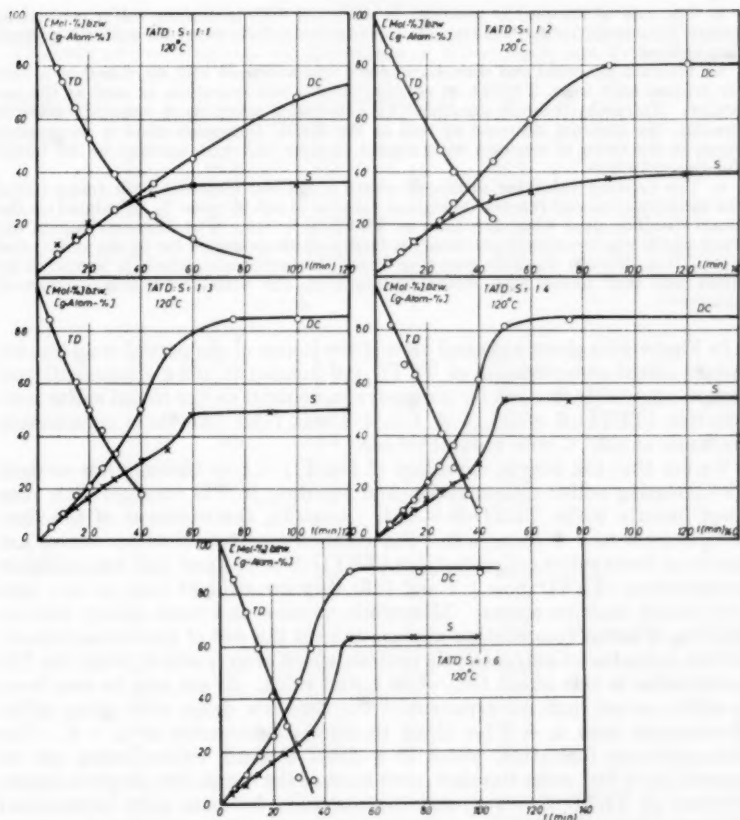


FIG. 44.—Decrease of thiuram disulfide (TD), increase of combined sulfur (S) and of zinc dithiocarbamate (DC) at various molar ratios of TD:S, (experiments with natural rubber with thiuram and ZnO constant and increasing S_8 concentration). bsw = respectively.

We can convince ourselves from the numerical data that the above equations are pretty well satisfied when we consider the range of vulcanization in which the thiuram concentration falls to about 20% of its original value⁶¹. Relations as they are given in the above equations are not met with any longer in sulfur vulcanizations accelerated by TD. What happens when increasing amounts of sulfur are used with thiuram disulfide will be discussed in the following section.

b. The vulcanization of natural and synthetic rubber accelerated by thiuram compounds⁶².—In the following we consider vulcanization accelerated by TD, to be the vulcanization of a 1,5 polyene by $\text{TD} + x\text{S}$ as well as by $\text{TM} + (x + 1)\text{S}$. Zinc oxide is also normally present.

The characteristics of this vulcanization which—as has been mentioned—actually belongs to the class of indirect crosslinking reactions, are as follows:

a. The rate of the partial reactions is increased with increasing sulfur content at constant TD concentration, yet the rate increase has a limit when the sulfur is present in large excess.

b. Thiuram decrease and dithiocarbamate formation are still expressed as a first order process only when TMTD, at constant initial concentration, is used as the accelerator. Tetraethylthiuram disulfide (TETD) reacts much more smoothly when it is present, the thiuram decrease as well as the ZnDC formation show a progressive increase in the order of reaction with respect to time (n_t) with increase in the initial sulfur concentration.

c. The limiting value for dithiocarbamate formation increases with rising initial sulfur concentration and reaches its highest value at about 90 mole %, calculated on the thiuram disulfide used when the ratio of TETD:S is 1:6. The dithiocarbamate deficiency which was mentioned previously is finally all compensated for by the sulfur, and nearly all the thiuram disulfide goes over into dithiocarbamate, which is formed in an amount like that found with direct reactions of TD with zinc oxide (reaction of Maximow⁶³).

In Figure 44 is given a general view of the course of the partial reactions for constant initial concentration of TETD (10 mmoles in 100 g compound) and constant zinc oxide content for successive increments in the initial sulfur concentration (TETD:S = 1:1, 1:2, 1:3, 1:4 and 1:6). All these experiments were made at 120° C with natural rubber.

We see that the convex curvature of the TD curves becomes less evident with increasing sulfur concentration and the drop in TD concentration runs almost linearly withn TETD:S = 1:4. Actually, the exponent of the time law falls from $n_t = 1$ to $n_t = 0$. The combined or bound sulfur curves are concave at lower sulfur concentrations (TETD:S = 1:1 and 1:2) but at higher concentrations (TETD:S = 1:4 and 1:6) they are straight lines, at any rate in the initial reaction stages. Meanwhile, a more and more clearly evident steep rise in sulfur combination appears toward the end of the vulcanization; and this indicates an autocatalytic process, which always sets in when the TD concentration is only about 10% of its initial value. It can also be seen from the sulfur curves that the exponent of the time law drops with rising sulfur concentration from $n_t = 1$ for direct thiuram vulcanization to $n_t = 0$. The dithiocarbamate formation, which in a direct thiuram vulcanization can be expressed by a first order time law, over most of the range, first shows a convex curvature at TETD:S = 1:2, and the convexity becomes more pronounced with increasing sulfur (DC Curves), which means that the autocatalytic process makes itself more and more evident in the early stages of the reaction, as the sulfur concentration is increased. We actually find negative exponents for the time law which is of course only a formal statement.

Furthermore, the points of intersection of the three curves again form a spherical triangle as was noted in Figure 42 for direct thiuram vulcanization, and the area of the triangle becomes larger and larger with increasing sulfur content and one of the angles finally coincides with the origin, which is evidently a result of the increasing sulfur concentration in these studies. On the other hand, the TD and DC curves always intersect at practically the same place; from this we may conclude, as before, that a close connection exists between thiuram decrease and ZnDC formation, at least as long as TD is present. Finally, it may be brought out that the poorly defined maximum in sulfur combination which appears in direct thiuram vulcanizations already at TETD:S = 1:1 is no longer apparent.

These experiments show that vulcanizations in which thiuram disulfides participate are very complex. Hence, it is very difficult to explain their complicated kinetic relations—for example, in the change of reaction order with respect to time.

TABLE XIII

DEPENDENCE ON REACTION TIME OF THE SUM OF THE TETD, ZNDEDC, AND BOUND S
CONTENT OF THE VULCANIZATE, EXPRESSED IN MG-ATOMS S, FOR VULCANIZATION
AT 120°C AND WITH VARIOUS RATIOS OF TETD:S

TETD:S	t, min	S _{TETD}	S _{ZNDEDC}	S _b	ΣS
1:0	0	40	—	—	—
	10	30.7	3.4	3.5	37.6
	15	27.7	4.8	4.2	36.7
	20	25.1	5.5	5.5	36.0
	30	21.2	7.5	6.9	35.6
	45	15.2	10.6	8.4	34.2
	60	11.8	12.4	9.5	33.7
	120	—	—	11.0	—
	∞	—	26.6	10.0	36.6
1:1	0	40	—	—	—
	8	31.7	3.5	6.0	41.2
	10	29.5	4.4	5.8	39.7
	15	25.7	5.7	7.7	39.1
	20	21.1	7.4	10.3	39.1
	30	15.5	10.6	12.8	38.9
	45	9.5	14.3	16.0	39.8
	60	6.0	17.9	17.4	41.4
	100	—	27.2	17.0	44.2
	∞	0	31.2	18.1	49.3
	ΣS _m = 39.7 (-0.75%)				
	<hr/>				
	0	40	—	—	—
1:2	5	34.3	2.2	4.0	40.5
	10	30.5	3.6	6.1	40.2
	15	27.3	5.4	8.1	40.8
	25	19.4	8.7	11.4	39.5
	30	15.9	11.2	14.2	42.3
	45	8.8	17.5	18.1	44.4
	60	—	24.0	19.4	43.4
	90	—	32.0	22.7	54.7
	∞	—	32.4	25.7	58.1
	ΣS _m = 40.3 (+0.75%)				
	<hr/>				
	0	40	—	—	—
1:3	5	33.7	2.2	3.7	39.6
	10	28.3	4.0	6.5	38.8
	15	24.1	7.0	8.7	39.8
	20	19.9	8.3	11.0	39.2
	25	16.8	11.0	14.4	42.2
	30	—	13.2	16.2	—
	40	7.0	20.0	21.6	48.6
	50	—	28.9	24.5	53.4
	60	—	33.8	33.6	67.4
	∞	—	33.6	35.4	69.0
	ΣS _m = 39.4 (-1.5%)				
	<hr/>				
	0	40	—	—	—
1:4	6	32.9	2.4	4.5	39.8
	11	26.9	4.6	6.7	38.2
	15	25.0	6.3	9.4	40.7
	20	20.7	9.0	12.3	42.0
	25	16.1	11.2	14.3	41.6
	30	11.2	14.5	17.1	42.8
	35	7.0	—	19.6	—
	40	4.8	24.5	22.4	51.7
	50	—	32.6	43.2	75.8
	∞	—	34.0	43.2	77.2
	ΣS _m = 40.4 (+1.0%)				
	<hr/>				
	0	40	—	—	—

TABLE XIII—Continued

TETD:S	t, min	S _{TETD}	S _{ZnDEDC}	S _e	ΣS
1:6	0	40	—	—	—
	5	34.0	2.5	4.6	41.2
	10	29.1	4.6	7.2	40.9
<hr/>					
	15	23.6	7.5	11.2	42.3
	20	16.4	10.5	15.8	42.7
	25	12.0	13.5	19.0	44.5
	30	3.8	18.6	23.1	45.5
	35	3.6	19.8	26.7	50.1
	50	—	35.3	62.5	97.8
	∞	—	35.2	63.1	98.3

Thiuram vulcanization is actually a model example of a complicated chemical reaction: at least three well-measurable partial reactions take place; intermediate compounds appear; the vulcanization can go as a heterogeneous catalysis when silica is present, although it is ordinarily not hetero-catalytic, only in case that zinc oxide is present, which on its part, in its reaction with thiuram disulfide, forms the chief reaction product in the vulcanization, namely zinc dithiocarbamate; the vulcanization with sulfur in the presence of thiuram disulfide is distinguished by a change in reaction order with respect to time, which is dependent on sulfur concentration; this at least is valid for the early stages, while an autocatalytic process of ZnDC formation and sulfur combination becomes more and more apparent toward the end of the vulcanization; and amid all the complications, the impression is always revived that a kind of stoichiometry of the reactions is maintained, because the limiting values for combined sulfur as well as for ZnDC are, as far as we can see, independent of temperature.

We can get more information about TD accelerated vulcanizations when we compare the material exchanges. This is done in Table XIII. In it, the vulcanizate's content of TETD, ZnDC and combined sulfur, S_e , are shown in their dependence on vulcanization time and for various ratios of TETD:S. The concentrations are expressed in mg-atoms of sulfur and are indicated by S_{TETD} , S_{ZnDC} , and S_e . In every case the initial concentration of TETD was 10 mmoles, so that $S_{TETD} = 40$. If the limiting value in a direct thiuram vulcanization is 66.6 mole per cent of the TETD used, then

$$S_{ZnDC} = 66.6 \times 0.4 = 26.6, \text{ etc.}$$

If we conceive the course of the vulcanization to be such that the TETD is finally all reacted and in so doing has gone over to ZnDC in part, (when the sulfur concentration is higher, the later transformation is nearly complete) while the free sulfur (S_f), the concentration of which also decreases toward zero, contributes on the one hand to raising the limiting value of ZnDC formation and on the other is taken up in stable combination by the rubber, then for a fully reacted vulcanizate, we must have:

$$(S_{ZnDEDC}) + (S_e) = (S_{TETD})_0 + (S_f)_0 \quad (35)$$

The right side of this equation represents the sum of the initial concentration of TETD and of free sulfur in mg-atoms of sulfur. Hence, at every instant of the vulcanization—we have:

$$(S_{TETD}) + (S_{ZnDEDC}) + (S_e) + (S_f) = (S_{TETD})_0 + (S_f)_0 \quad (36)$$

However, if a certain portion of the total sulfur remains undetermined in the form of soluble compounds in the extracts of the vulcanizate, as happens even for the fully-reacted direct thiuram vulcanization, then we will have:

$$(S_{TETD}) + (S_{ZnDEDC}) + (S_g) + (S_l) + (S_t) = (S_{TETD})_0 + (S_t)_0 \quad (37)$$

Now we must note that neither the concentration of residual free sulfur (S_t) nor of (S_l) is known. Therefore we must confine ourselves to closer examination of the sum of (S_{TETD}), (S_{ZnDEDC}) and (S_g).

$$\sum S = (S_{TETD}) + (S_{ZnDEDC}) + (S_g) \quad (38)$$

This summation is given in Column 5 of Table XIII.

It is seen that in a direct thiuram vulcanization (TETD:S = 1:0), the value of $\sum S$ never reaches 40, even in the fully reacted vulcanizates. For $t = \infty$ we find $\sum S = 36.6$, and that means that 3.4 mg-atoms S, corresponding to 0.85 mmole or 8.5 per cent of the initial concentration of TETD is still unaccounted for. When TETD:S = 1:1 to 1:6 the expected value for sulfur in the com-

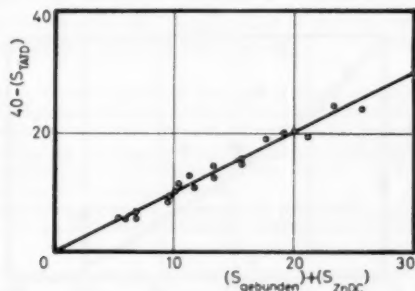


Fig. 45.—Relationship between reacted thiuram disulfide and the sum of the combined sulfur plus zinc dithiocarbamate in vulcanizations accelerated with TETD.

pletely reacted vulcanizate is reached quite nicely, so that Equation 38 is satisfied and hence we should conclude that all the sulfur in a TD accelerated vulcanization finally goes into ZnDEDC and combined sulfur, and there are no unidentified sulfur compounds⁶⁴.

We can also find in Table XIII that $\sum S$ remains constant and keeps the value of 40 that is calculated from the initial concentration of TETD until the TD concentration begins to fall below half of its initial value. In this first half of the reaction, which is divided from the rest by the horizontal dotted lines in the Table, the following must apply:

$$(S_{TETD}) + (S_{ZnDEDC}) + (S_g) = (S_{TETD})_0 = 40 \quad (39)$$

and hence

$$(S_{TETD})_0 = (S_{TETD}) = 40 - (S_{TETD}) = (S_{ZnDEDC}) + (S_g) \quad (40)$$

Because these equations never apply for direct thiuram vulcanization, even in the first half of the reaction, it seems that the free sulfur which is present smooths out the picture of the reaction, even if it must always be emphasized that these relationships are found only as long as the TETD concentration is

high enough to control the process; and we can also see that the dithiocarbamate, which is a most effective accelerator in its own right, displays no catalytic activity in the vulcanization, in any case during the half transformation of TD. If that were not the case we could not understand why, in the range of reaction here considered, and as shown in Figure 45, a proportionality exists between $40 - (S_{TETD})$ and $[S_g] + (S_{ZnDEDC})$ (see Equation 40), and why a correlation (which is independent of the ratio TETD:S) is found between TETD which is still present and the ZnDEDC which is formed, (see Figure 46).

2. *Vulcanization by peroxides.*—It is well known that natural rubber as well as synthetic rubbers can be vulcanized by some peroxides. The process itself as well as the physical-technical properties of the vulcanizates have been frequently studied⁶⁵. The process occurs at greatly differing rates depending upon the chemical constitution of the peroxides; under certain circumstances crosslinking takes place by the time a peroxide is blended with the rubber. Because the peroxides promote the formation of C—C bridges between polymer chains, this vulcanization also has a certain technical interest, for such vulcanizates should be inherently more stable toward oxygen than elastomers crosslinked with sulfur. However, the physical-technical properties, particularly the

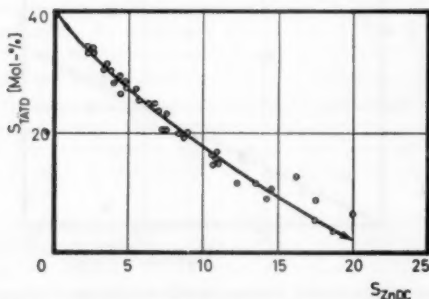
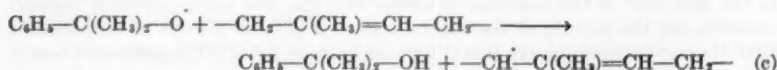
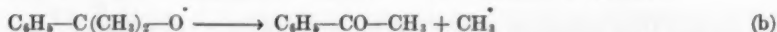
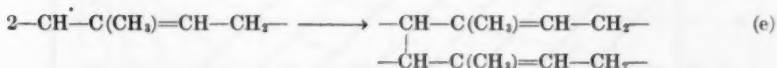
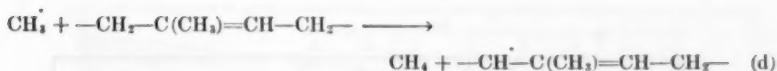


Fig. 46.—Relationship between free thiuram disulfide and zinc dithiocarbamate formed in vulcanizations accelerated with TETD (varying molar ratio TETD:S).

tensile strength, are not always satisfactory. As a general rule, the properties will be better the smaller the amount of peroxide added for the vulcanization. Dialkyl peroxides⁶⁶ and percarbonate esters⁶⁷ give better vulcanizates than dibenzoyl peroxide. The smoothly reacting and safe dicumyl peroxide has found especial interest; it is even able to crosslink polypropylene.

Peroxide vulcanization has considerable scientific interest; in many cases, the fundamental chemical reaction is relatively simple and clear, so that the connection between chemical change and the linking together of macromolecules is clearer than it is in sulfur vulcanizations. This is true for vulcanizations with dicumyl peroxide, which, according to the literature⁶⁸, should go as follows:





It can be seen here that the cumyloxy radical and the methyl radical which appear in Equation (b) attack only the methylene group, forming either dimethyl benzylalcohol or methane and do not at all affect the double bond in the polymer chain. The resulting resonance-stabilized polymer chain radicals then should combine as shown in Equation (e), and thus cause crosslinking. According to this scheme, a crosslink site appears for each molecule of the peroxide.

The probability of this was established recently by Parks and Lorenz²⁰, who investigated the reaction of dicumyl peroxide with 2,6-dimethyl-2,6-octadiene. They were able to identify the dimer of the diene and isolate it in the expected amounts.

We found that the kinetics of vulcanization of natural rubber⁷⁰ is in complete agreement with the above reaction mechanism:

1. The decrease in concentration of dicumyl peroxide proceeds according to a first order time law at all temperatures and initial peroxide concentrations. An activation energy of 36 kcal/mole is calculated from the temperature dependence of the rate constant. Figure 47 shows the decrease of concentration in a plot according to a first order time law, for the temperature range from 120° to 155° C; the initial concentration of peroxide was 10 mmoles/100 g compound.

2. The rate constants of peroxide decrease are practically independent of the initial peroxide concentration, as is seen in Figure 48. Curves I to VIII with initial concentra-

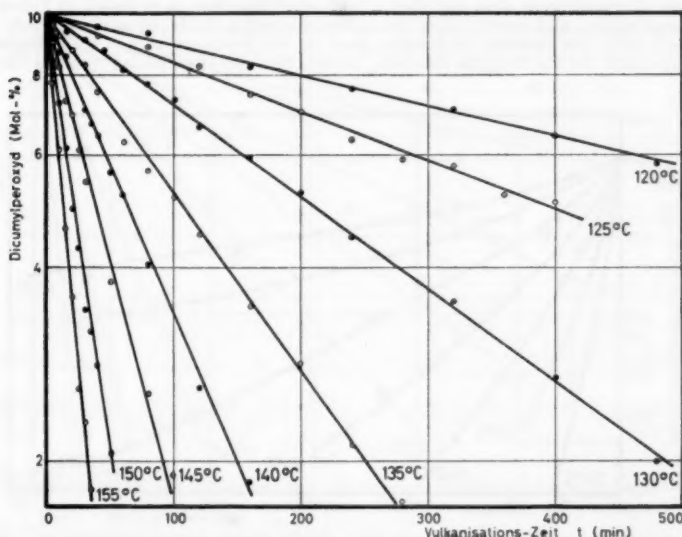


Fig. 47.—Concentration decrease of dicumyl peroxide in natural rubber at various temperatures, according to a first order reaction (initial concentration 10 mmoles/100 g compound).

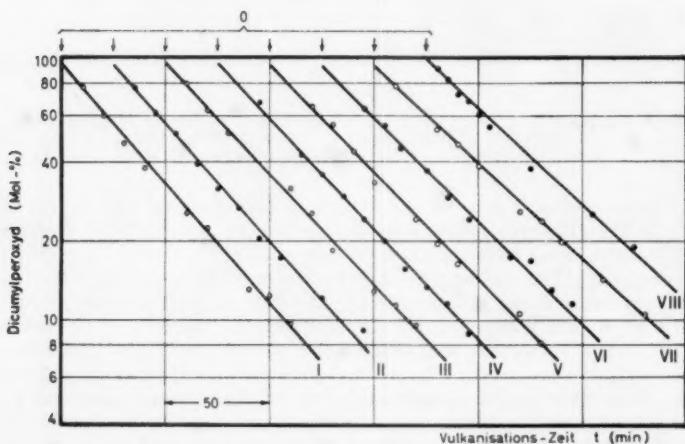


FIG. 48.—Concentration decrease of dicumyl peroxide in natural rubber for increasing initial concentrations of peroxide (VIII-I: 10, 15, 20, 25, 30, 35, 40, and 45 mmoles per 100 g compound).

tions of 45, 40, 35, 30, 25, 20, 15 and 10 mmoles peroxide in 100 g of compound are sufficiently parallel. From this we must conclude that the decomposition of dicumyl peroxide follows a monomolecular reaction and hence is homolytic. This is in agreement with the results of an investigation by Kharasch and coworkers⁷¹, who showed, moreover, that the decomposition of dicumyl peroxide takes place at practically the same rate in all the solvents which they used. The rate of decomposition in natural rubber in our work is in good agreement with these results.

3. The change with time of the reciprocal equilibrium swelling, which represents a measure of crosslinking, does not obey a first order time law, as is shown in Figure 49. But recalculation and correction of the values according to the equation of Flory and Rehner⁷², with the insertion of a value given in the literature of $\mu = 0.43$ (benzol as swelling agent) for the Huggins constant, showed that the crosslinking reaction likewise

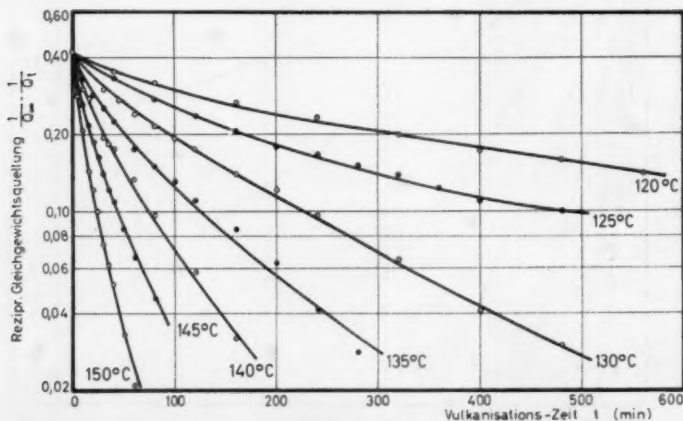


FIG. 49.—Dependence of the reciprocal equilibrium swelling upon the reaction time at various temperatures (vulcanization of natural rubber with dicumyl peroxide, 10 mmoles/100 g compound).

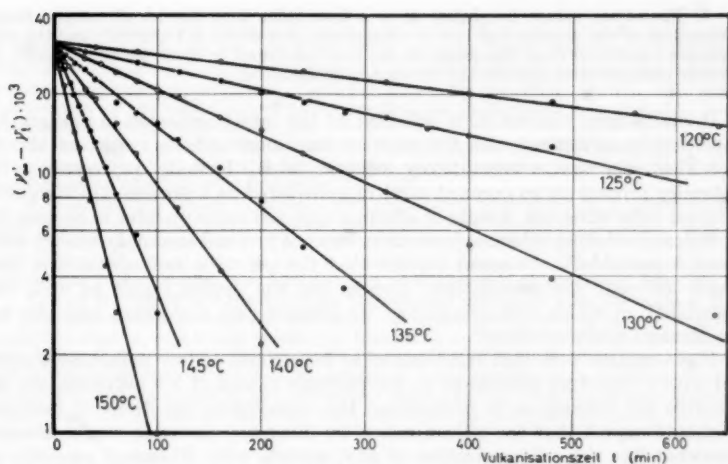


FIG. 50.—Increase of crosslinking according to a first order reaction for the vulcanization of natural rubber at various temperatures with 10 mmole dicumyl peroxide in 100 g compound. (Ordinates: proportional to the number of crosslink sites ν' .)

follows a first order time law. This is shown in Figure 50, where values proportional to the number of crosslink sites calculated with the Flory and Rehner equation are plotted according to a first order time law for different temperatures. The rate constants calculated from the slopes of the straight lines which were obtained are the same as those for the decrease of the peroxide at the same temperatures, which indicates that crosslinking and decrease of peroxide are processes with equal rates, and the homolysis of the peroxide represents the rate determining step.

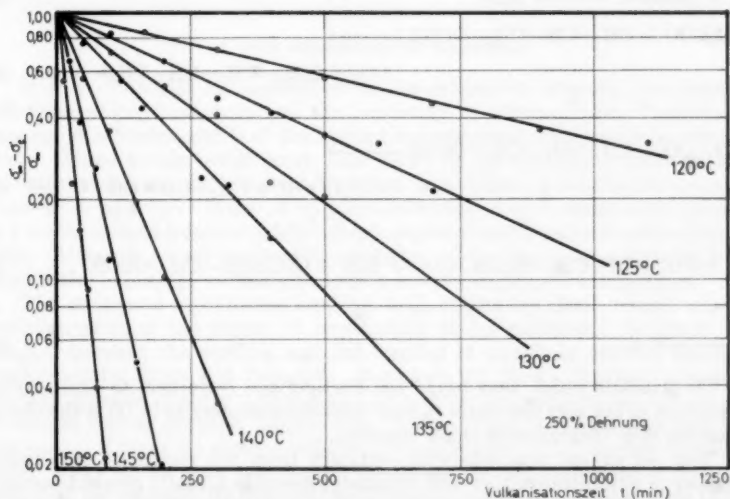


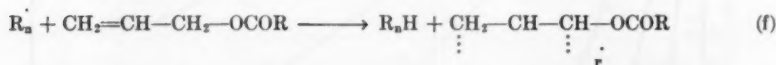
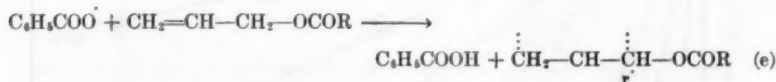
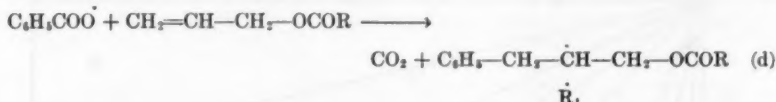
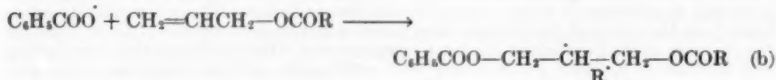
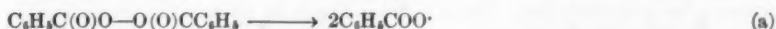
FIG. 51.—Increase of the stress values according to a first order reaction for the vulcanization of natural rubber with dicumyl peroxide at various temperatures. Dehnung—extension.

4. The stress values (modulus) obey a first order time law at all temperatures, independent of the amount and rate of elongation, as is shown in Figure 51; and the rate constants calculated from the slopes of the lines are equal to those for the decrease in peroxide concentration and for the increase in crosslinking.

It can be seen without more ado that all the results collected in paragraphs 1 to 4 are in agreement with the reaction mechanism which was given above. It is also clear that a crosslinking reaction, which formally represents a bi-molecular process on no account must be considered as a process which follows a second order time law, a state of affairs which will come up later in Section D.

Vulcanization by dibenzoyl peroxide does not proceed so simply as that with dicumyl peroxide⁷³. It seems certain that the peroxide radicals in this case attack not only the α -methylene groups, but the double bonds as well, the probability of which was established by Farmer and coworkers and also by van Rossem and coworkers⁷³.

If we assume now that reactions of hydrocarbons of low molecular weight and with a structure analogous to the polymer chains of 1,5 polyenes, are instructive for helping us to understand the crosslinking reactions of rubbers, we should expect that the vulcanization by dibenzoyl peroxide would proceed somewhat like the polymerization of allyl acetate with dibenzoyl peroxide as initiator, which was studied in more detail by Bartlett and coworkers⁷⁴. They considered their results to be in agreement with the following reaction mechanism⁷³:



The kinetics which were found led Bartlett and coworkers to assume that a reaction of the polymer chain radical with the monomer as in (f) is the chain-breaking step (degradative chain transfer).

Now we cannot conclude with certainty from the results of our studies whether or not vulcanization with dibenzoyl peroxide actually proceeds according to the above scheme since the crosslinking reaction up till now has not been measured. Still, we found⁷⁵ the following results which actually are to be expected from the above scheme.

1. Vulcanization by dibenzoyl peroxide is easily followed analytically in the range of temperatures between 50° and 110° C. It proceeds faster than that with dicumyl peroxide. The concentration decrease of the peroxide obeys a first order time law for all temperatures and concentrations which are below the saturation point. The rate is independent of the initial concentration so that the decomposition is probably homolytic, corresponding to Reaction (a).

2. A certain amount of benzoic acid is formed during the vulcanization, evidently in a manner like that shown in Reaction (e) of the preceding scheme. The benzoic acid formation also follows a first order time law.

3. The limiting values of benzoic acid production were found to be dependent on temperature but not on concentration. We determined 60, 55, 48, 47 and 45% of the acid, calculated on the amount of peroxide used at temperatures of 50°, 60°, 75°, 90° and 110° C respectively; so there is noted a considerable decrease in the amount of benzoic acid formed with rising temperature, surely a consequence of the course of Reaction (d).

4. The first order rate constants for benzoic acid formation were the same as those for peroxide decrease only at 50° and 60° C; at higher temperatures they were always somewhat smaller, which may possibly be blamed on an increasing effect of Reaction (d) with rising temperature. The approximate equality of the rate constants, however, can be looked upon as evidence of the existence of two simultaneous reactions, namely: on the one hand the attack of the benzoyloxy radical on the α -methylene groups according to Reaction (b) and on the other hand the attack on the double bonds according to Reaction (e).

The results collected in paragraphs 1 to 4 are still not adequate by themselves for the formulation of a detailed reaction mechanism. But if we examine the mechanism as it was proposed for the polymerization of allyl acetate induced by dibenzoyl peroxide, we see that the results at any rate are by no means in contradiction to it. Without question the homolytic splitting of the peroxide according to Reaction (a) is the rate determining step. So the formation of benzoic acid obeys the same time law as the peroxide decrease. As we should expect, its rate, like that of the peroxide decrease, is independent of the initial peroxide concentration, and, at least for lower temperatures, is the same as that for the decrease of peroxide.

D. THE CROSSLINKING REACTION

It is obvious that an explanation of the connection between the chemical reactions which take place and the formation of intermolecular bridges has especial significance and is of the highest importance from a practical point of view. These bridge bonds exert their effect in the changes in physical and technical properties, such as in the increase in modulus values and the decrease in swelling capacity. It should be possible to subject the vulcanization process to a mathematical treatment, when these relations have found a kinetic clarification. Although we are engaged in answering all the questions connected with this, in the following, we will give only a few of our present conceptions.

The reciprocal equilibrium swelling $1/Q$, of and by itself, should give a useful measure of the degree of crosslinking in 1,5 polyenes. However, the relation between the swelling and the number of crosslinks present was first established by Flory and Rehner⁷². But since the theory does not take into account possible changes which may occur in the constitution of the macromolecules such as certainly happen with vulcanization by means of sulfur, it is not certain if it can be applied, without reservations, to the processes discussed here. Thus far we have called upon the theory for the evaluation of swelling data only for vulcanizates prepared with dicumyl peroxide. (See Section C, 2.) In that work it appeared that the peroxide decrease and the crosslinking are first order reactions with practically the same rates. However, it follows from this that a crosslinking reaction, which as such represents a bimolecular reaction,

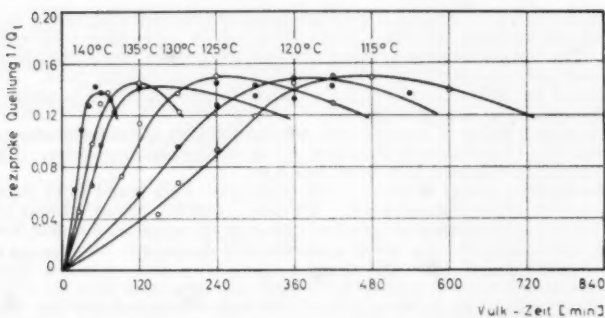


FIG. 52.—Increase of the reciprocal equilibrium swelling for the vulcanization of natural rubber by sulfur in the presence of MBTS at various temperatures (concentration of the reactants 100 mmoles/100 g compound).

must not be considered absolutely, as a second order process, which means that molecularity and order of reaction need not be the same here.

Further difficulties in the quantitative treatment of the crosslinking processes arise with respect to the evaluation of the swelling and modulus measurements themselves, which may be demonstrated with a few examples.

Figure 52 shows the increase of $1/Q$ with the vulcanization of natural rubber with sulfur in the presence of MBTS at various temperatures. All of the curves show a well defined maximum which is evidently only slightly dependent on temperature, and which is shifted into the range of longer reaction times with lowered temperature, all of which is an expression of the well known phenomenon of reversion. Moreover, the curves have an S-shape. It is difficult to decide if they actually run into the origin—as is shown here—since swelling measurements for low degrees of crosslinking are hard to carry out or are too inexact to permit a decision on this point.

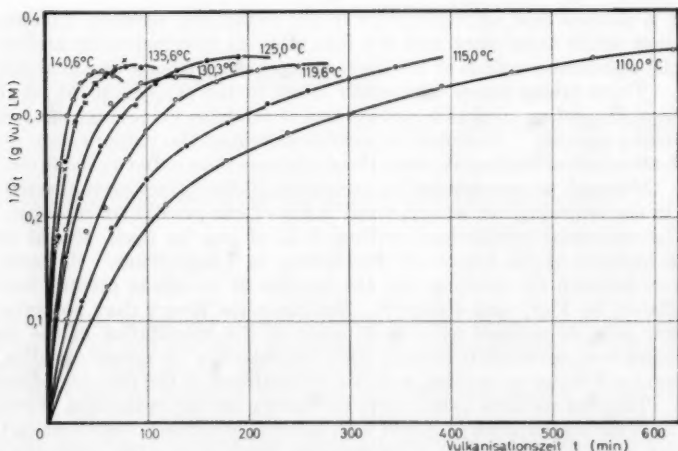


FIG. 53.—Increase of the reciprocal equilibrium swelling for the vulcanization of natural rubber by sulfur in the presence of DPG and ZnO (concentration of S_8 , accelerator 10 mmoles in 100 g compound).

On the other hand, we may assume that the curves in Figure 53 do start at the origin. These curves are for the vulcanization of natural rubber with sulfur in the presence of DPG and zinc oxide. In this case, reversion is much less evident, especially, of course, at lower temperatures.

Finally, it is shown in Figure 54, for the vulcanization of natural rubber with dicumyl peroxide, that the increase of the stress values with vulcanization time shows scarcely any reversion. This is observed independently of elongation and of rate of elongation and is observed also at temperatures other than 140°C.

These few examples indicate that the dependence of crosslinking on the vulcanization time—whether it is measured by swelling or by stress values—gives very distinctive graphs.

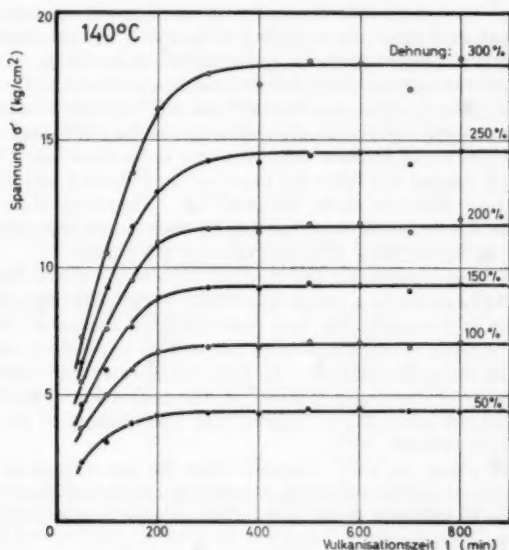


Fig. 54.—Increase of the stress (Spannung) values for the vulcanization of natural rubber with dicumyl peroxide. Dehnung = extension.

As long as no reversion exists, or only a trivial amount, as is the case with thiuram vulcanizates (direct thiuram vulcanization), the kinetic evaluation of the curves offers no great difficulty. At any rate the limiting value of the crosslinking (σ_∞ or $1/Q_\infty$) can then be obtained with some degree of accuracy. This is done, for instance, by plotting $\log \sigma$ or $\log 1/Q$ against the reciprocal of the reaction time and extrapolating the curves to $1/t = 0$. Moreover, if we may assume that the limiting value of the crosslinking is independent of temperature for a given concentration of reactants, the extrapolation will gain in accuracy, if a set of curves for different temperatures is available, so that a set of converging curves is obtained by plotting σ or $1/Q$ against $1/t$, and their point of intersection for $1/t = 0$ can easily be determined.

However, if reversion occurs, which is of course always the result of two concurrent reactions, we can speak only of an estimate of the limiting value of the reciprocal equilibrium swelling or of the stress, even if we have available a

set of curves for different temperatures. If we have only a single curve at hand ($T = \text{const}$), the determination of the limiting value is fraught with much uncertainty in the presence of reversion. In any case, the determination of the limiting value is all the more complicated and questionable the more pronounced the reversion and the earlier it appears. It is clear from what has been said that we can easily find too small a limit.

The diagnosis is made all the more difficult by the fact that the values for the stress as well as for the reciprocal equilibrium swelling are measured only with great difficulty or very inaccurately for small degrees of crosslinking. As a result of this the path of the curves for the early stages of reaction is quite uncertain, and under certain circumstances, any induction periods which occur are hard to recognize and to diagnose.

Experience teaches us that the order of reaction with respect to time (n_t) depends a great deal upon the accuracy with which we can or have measured the end value of the stress or reciprocal equilibrium swelling.

An eloquent example of this is the evaluation, undertaken by Craig², of the measurements made by Gee and Morrell⁴¹, on the increase of stress in the vulcanization of natural rubber in the presence of ZnMBT and zinc stearate. While the authors could fit their data to a first order time law, Craig found, in a case which he singled out, that the crosslinking follows a second order course when he used an ultimate stress value of 8.0. However, if he used smaller values, such as 7.8 or larger, such as 8.5, he then found important deviations from a second-order course. Such experiences are common.

In light of these circumstances, in what follows we would like to make an effort merely to examine, in a rough quantitative way, the dependence between sulfur decrease and crosslinking in a few examples chosen at random and to consider the half-life times, since they are not as dependent on the limiting values as is the order of reaction. In this, we have at first consciously disregarded the theory of Flory and Rehner⁷² in the evaluation of swelling measurements, but without intending to express any underrating of the concepts developed by these authors.

In the first place, we may consider what we can expect in general with respect to the kinetics of crosslinking, drawing upon the results of kinetic studies on the decrease of sulfur in direct and indirect vulcanizations which have been given in previous Sections.

Direct vulcanization (Section III, A) was recognized as a first order reaction with respect to sulfur, and as such, due to the excess of structural units of rubber present, may be a pseudo-monomolecular process. Now if we assume that sulfur is always combined with a simultaneous resulting formation of bridge bonds, the crosslinking reaction should have the same rate as the decrease of sulfur and its order of reaction should then also be the same. If this is not the case, and sulfur is combined at first "ineffective for crosslinking", so that it must be regarded as an intermediate as far as crosslinking is concerned, then the crosslinking and sulfur decrease cannot have the same rate nor a single order of reaction with respect to time. But even if a time law can be laid down under these circumstances, it cannot be second order, again because of the excess of rubber and its structural units. Similar relations hold for accelerated vulcanization, where—as the kinetics of the sulfur decrease make probable—an intermediate product occurs, which reacts with rubber in a formal bimolecular process, which determines the rate of sulfur decrease. Also, under these conditions, the crosslinking—in so far as the reaction of the sulfur results in the formation of bridges—cannot be of the second order, because of the great excess

TABLE XIV

HALF-LIFE TIMES OF SULFUR DECREASE AND OF CROSSLINKING IN DEPENDENCE ON TEMPERATURE IN THE REACTION OF NATURAL RUBBER WITH SULFUR (12.5 mmoles S_8 in 100 g; $1/Q_\infty = 0.20$)

Temperature, °C	Half-life times of sulfur decrease, min.	Half-life times of $1/Q$, min
140	295	274
145	186	164
150	128	112
153.8	74	88
160	52	68

of rubber. In spite of such considerations it is always advisable to let the decision rest with the experimental results.

We next examine the decrease of sulfur as well as the increase of $1/Q$ for the direct vulcanization of natural rubber (12.5 mmoles S_8 in 100 g) at various temperatures. It is found here that in the range of reaction times used reversion is evident about 150°C. The end value for swelling, $1/Q_\infty$, was found to be 0.20. The half-life times of sulfur decrease and of crosslinking are compared in Table XIV.

TABLE XV

HALF-LIFE TIMES OF SULFUR DECREASE AND OF CROSSLINKING FOR THE VULCANIZATION OF NATURAL RUBBER AT 150°C AS A FUNCTION OF THE INITIAL SULFUR CONCENTRATION

Initial concentration of sulfur, mmoles S_8 /100 g	Half-life time of sulfur decrease, min	$1/Q_\infty$	Half-life times of $1/Q$, min
6.25	110	0.076	88
12.5	126	0.154	72
18.75	131	0.17	73
25.0	120	0.23	95
37.5	127	0.37	88
50	113	0.56	114
62.5	115	0.83	(160)

When we consider that we must count on variations in degradation or breakdown of the rubber, in spite of the most careful control of temperature and time in the mastication and mixing processes, and that these variations should exert an effect on the apparent limiting value of the crosslinking, and considering that the determination of $1/Q_\infty$ is no easy task, we can speak of a satisfactory agreement in the half-life times which were found in this series of experiments. In any case, the results give no inducement for deducing that sulfur decrease and crosslinking are processes not connected with each other.

TABLE XVI

HALF-LIFE TIMES OF SULFUR DECREASE AND OF CROSSLINKING IN DEPENDENCE ON THE TEMPERATURE AND WITH ZINC OXIDE PRESENT (Sulfur = 12.5 mmoles S_8 /100 g; ZnO = 50 mmoles in 100 g; $1/Q_\infty = 0.20$)

Temperature, °C	Half-life time of sulfur decrease, min	Half-life time of $1/Q$, min
140	285	285
145	170	190
150	116	122
155	77.5	83
160	47.5	60

TABLE XVII

HALF-LIFE TIMES OF SULFUR DECREASE AND OF CROSSLINKING IN DEPENDENCE ON THE INITIAL CONCENTRATION OF SULFUR AND WITH ZINC OXIDE PRESENT FOR THE VULCANIZATION OF NATURAL RUBBER AT 150°C

Initial sulfur concentration, mmols S ₈ /100g	Half-life time of sulfur decrease, min	1/Q _∞	Half-life time of 1/Q, min
6.25	100	—	—
12.5	111	0.156	90
18.75	124	0.228	90
25	118	0.263	80
37.5	112	0.375	86
50	94	0.50	86

The corresponding results for a constant temperature of 150°C and for varying initial sulfur concentration may now be examined. In this connection, for the time being, only a single curve, is available for evaluating the end value of the crosslinking so the interpretation is quite difficult. The estimated half-life times are given in Table XV, along with those for the sulfur decrease.

It has been pointed out already in Section III, A, 1b, that the half-life times of sulfur decrease are independent of the initial sulfur concentration and indicate a reaction of the first order. In the case of this series of experiments, we might think that the half-life times of sulfur decrease are thrown in at random, for they show no correlation with the concentration. The same might be said also for the half-life times for crosslinking, if we ignore the value of 160 which was found for 62.5 mmols of S₈. However, we see that the half-life times of

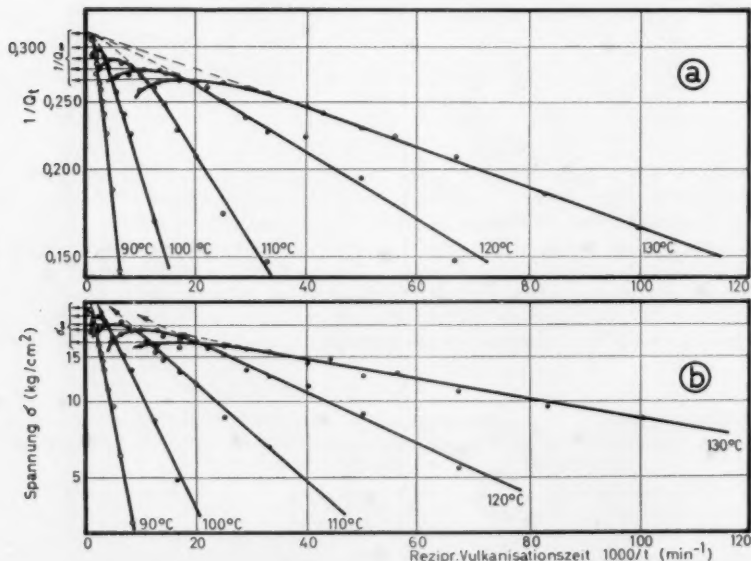


FIG. 55.—Reciprocal equilibrium swelling, (a), and stress, (b), as functions of $1/t$ for the vulcanization of rubber with sulfur in the presence of ZnMBT and zinc stearate.

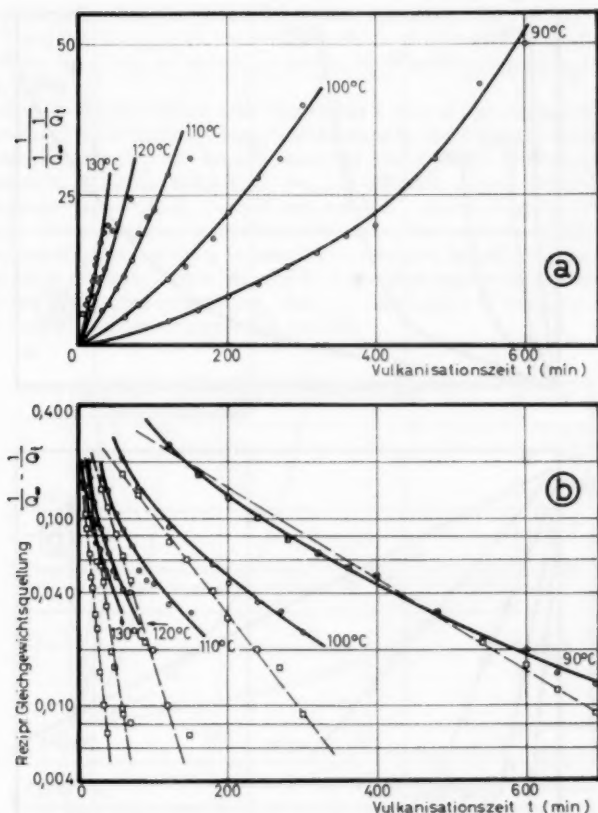


Fig. 56.— $1/Q = f(t)$ displayed according to second order, (a), and first order, (b), with the assumption of constant ultimate values from Figures 55a.

$1/Q$ are altogether smaller than those for sulfur decrease. That could lead to the assumption that the crosslinking proceeds more rapidly than the decrease of sulfur concentration, which is hardly possible. However, it has been pointed out already that it is easy to find limiting values of crosslinking which are too small; and, of course as a consequence, the half-life times are correspondingly lowered. But in spite of this, the data do not argue against a connection between the sulfur decrease and the crosslinking, especially since we can appraise the constancy of the half-life times, which is notable over a considerable range of sulfur concentrations, as an indication that the crosslinking process is a first order reaction ($n_e = 1$).

The experiments which are next described were made with zinc oxide also present, and as Tables XVI and XVII show, the same relations are found.

We might now consider the case of the vulcanization of natural rubber by sulfur in the presence of ZnMBT and zinc stearate since it was also investigated in another connection⁷⁶ as an example of an indirect vulcanization. It may be

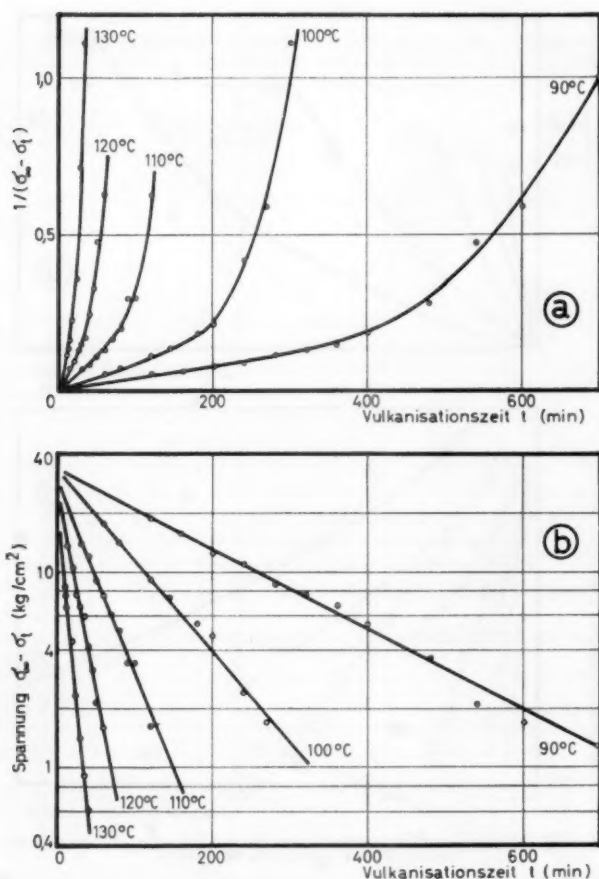


Fig. 57.— $1/Q = f(t)$ displayed according to second order, (a), and first order, (b), while assuming various ultimate values from Figure 55a.

recalled (see Section III, B, 5, b) that the sulfur decrease in this vulcanization was found by Lorenz and Echte to be always in agreement with a first order time law.

The kinetics of crosslinking was also investigated by Martin, Roth and Stiehler⁷⁷, whose work was mainly based on measurements of the increase in modulus. Craig² found that the results of these authors also fitted a second order time law. Measurements of the reciprocal equilibrium swelling by Lorenz and Echte³⁹, were likewise interpreted by Craig as following a second order process, while the authors themselves found equality of the rate of sulfur decrease and the increase with time of the reciprocal equilibrium swelling according to the first order. This is in agreement too with the interpretation of Gee and Morrell⁴¹, who found the increase in the modulus values for this vul-

canization reaction to agree with a first order time law. Yet, as has been mentioned, Craig was able to fit the measurements of Gee and Morrell also to a second order time law, of course by choice of suitable ultimate values of the modulus.

We show in the first place with Figure 55a a plot of $\log 1/Q$ against $1/t$ and see immediately that there are two possible ways to carry out the extrapolation. If we extrapolate along the broken lines, we find a single ultimate value. If we extrapolate along the solid lines, we find ultimate values which depend on the temperature, and which, over all, are smaller. It is difficult to judge which is correct. If we establish a constant end value, the increase with time of the reciprocal equilibrium swelling cannot be represented by either a first order or a second order process, Figure 56a and b; if we have regard for the smaller and temperature dependent end values, then we find $1/Q$ is of the first order and not of the second order (Figures 57a and b).

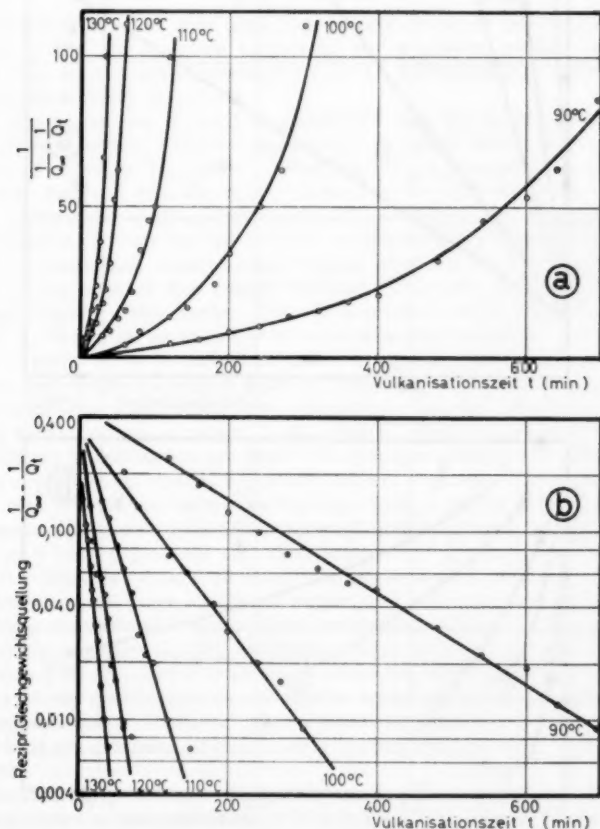


FIG. 58.—Increase of the stress values according to the second order, (a), and to the first order, (b), while assuming various ultimate values from Figure 55b.

Things are the same when we determine the limiting stress values. We again have two possible ways for extrapolation as Figure 55b makes clear. If we choose the smaller and temperature-dependent end values, then we find the increase with time of the stress values proceeding not according to a second-order but perhaps according to a first-order law, Figures 58a or b, and there is equality of rate with the increase in the reciprocal equilibrium swelling. However, if we consider the ultimate values obtained by linear extrapolation of the curves, then the rise of the stress values does not follow a first order time law, Figure 59b, but agrees much better with a second order course (Figure 59a) so that there is agreement with the measurements of Martin, Roth and Stiehler⁷⁷.

We see that $1/Q = f(t)$ cannot be expressed by a second order law in any case, and only follows a first order process when we use the smaller, temperature-

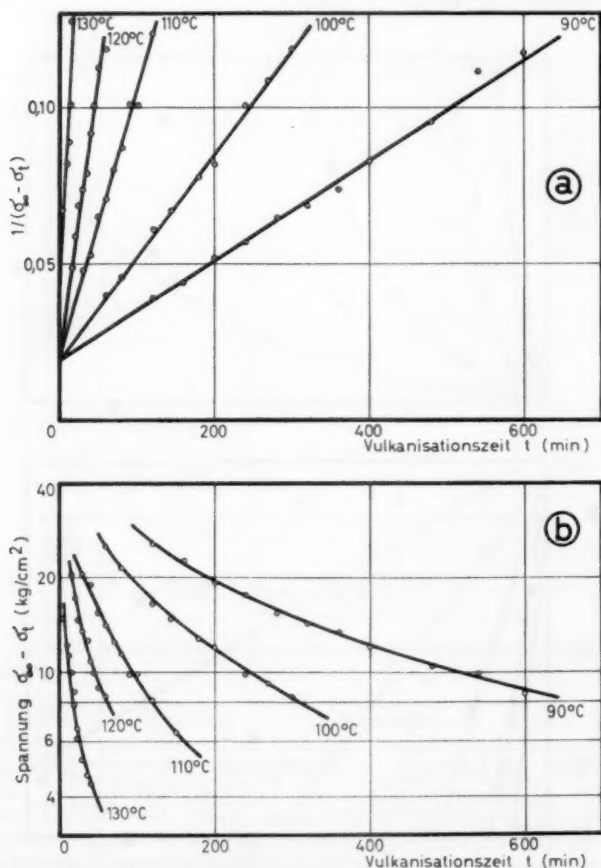


FIG. 59.—Increase of the stress values according to second order, (a), and to first order, (b), based on the linear extrapolated ultimate values from Figure 55b.

dependent end values, in which case, $\sigma = f(t)$ also is of the first order. We find a second-order time law in effect for the stress increase only with a linear extrapolation; but in that way end values are introduced which are not found at all experimentally; this is shown by an analysis of the reaction curves (not shown here).

Of course the objection may be raised that it is not permissible to use the values of $1/Q$ directly for such considerations, that, on the contrary it is absolutely necessary to consider the number of crosslinks which is calculable from the Flory and Rehner equation. Yet it must be emphasized that the difficulty encountered in the determination of limiting values is not overcome in this way.

Relations found in other cases are similar to those given in the examples just discussed. So it seems that in no case yet can the question of the order of reaction and rate of the crosslinking process be positively decided.

IV. CONCLUDING CONSIDERATIONS

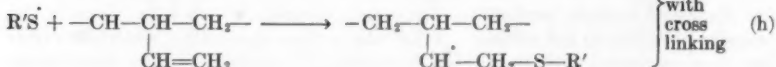
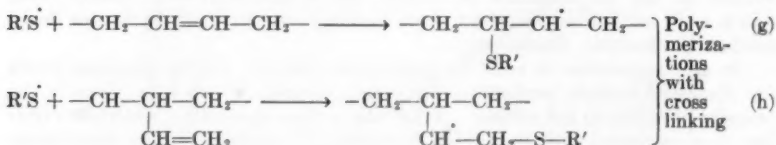
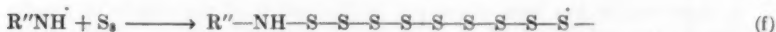
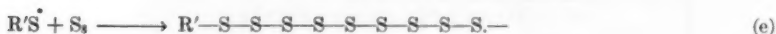
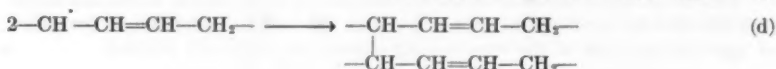
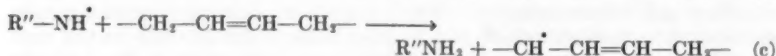
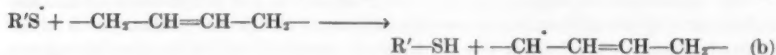
A short review has been presented in this article of the results of kinetic studies on the vulcanization of natural and synthetic rubber, chiefly those which were carried out in recent years at the Kautschukinstitut an der Technischen Hochschule, Hannover.

In this connection it must be considered that the kinetic relations which are discussed include predominantly those processes which take place in the transfer of sulfur to the rubber. What takes place thereafter, when the sulfur has once combined with the rubber, is summarily expressed in the dependence of the polysulfidic combined sulfur on reaction time. But in the background are concealed all those reactions which are instructively treated, since Farmer, in the distinguished experimental organic chemical studies performed with model compounds at the British Rubber Producers' Research Association, Welwyn Garden City, Herts. But, in accordance with the selection of our theme, these studies could not be entered into here in detail.

It is fundamental to their nature that kinetic methods alone cannot always provide sufficient argument in order to formulate a reaction mechanism which is justifiable and which stands firm against all criticism. So the reader of this article should not be surprised if the possible chemical reactions which take place during vulcanization are dealt with rather sparingly, and emphasis is put on the experimental results, which after all are decisive. He might, of course, think that it does not take a particularly keen mind to write down reaction schemes which should make the course of a vulcanization reaction plausible, using as a basis experience with the chemistry of low molecular weight compounds. What is actually necessary though is to pick from a large number of possible reactions, those which are cogent and which really take place. Now if a study of reaction kinetics and its results cannot answer such a question by themselves nevertheless the assertions which they permit are in general so constituted as to make it possible to stake out the framework within which further purely chemical studies should be made, which will then lead closer to the fundamentals. If this article is examined more closely and the many facts given in it are pondered, it will be seen that in this respect it contains a series of hints.

We assume, for example, that sulfenamides in every case undergo a radical decomposition at the start whether it be in the crosslinking of synthetic rubbers which contain vinyl side groups or in acting as an accelerator in indirect vulcanizations with sulfur. All further reactions should be initiated by this de-

composition which is shown in Reaction (a). It is—at any rate provided sulfur is present—always characterized by a well-defined induction period which depends on the constitution of any particular sulfenamide.



Poly-
meriza-
tions
with
cross
linking

There is a series of reaction possibilities for the radicals shown in Reaction (a). For instance, they can react, as shown in Reactions (b) and (c), with the α -methylene groups of the structural units of 1,5 polyenes, forming resonance stabilized polymer chain radicals and amine and mercaptan; crosslinking according to Reaction (d) may then follow. Amine and thiazole thiols supposedly existing as salts will act as accelerator if sulfur is present. The radicals formed in Reaction (a) can also react with sulfur according to Reactions (e) and (f) and the persulfenyl radicals will then react with the vulcanizate. Finally there is the possibility of a polymerization being induced by the radicals according to Reactions (g) and (h), in which the excitation of the vinyl group in synthetic rubbers according to Reaction (h) is much more probable than that of the double bond of the polymer chain shown in Reaction (g); for sulfenamides alone give no crosslinking in natural rubber. All these reactions may be discussed as processes which initiate vulcanization or its acceleration.

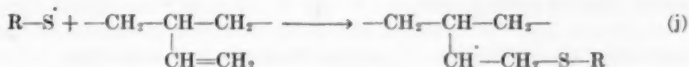
Now on the other hand, kinetic investigations of vulcanization of natural rubber with sulfur accelerated by sulfenamides have shown that the decomposition of the sulfenamide which always starts suddenly is accompanied by crosslinking which also sets in just as suddenly, and which always declines again when the sulfur begins to react in the manner characteristic of accelerated vulcanizations. This is noteworthy. In our opinion, none of the Reactions (a) to (f) can explain this "artificial" reversion, and there is also no explanation here as to why the concentration of sulfur sometimes decreases at the same rate and according to the same time law when we use an equivalent amount of the substituted ammonium salt instead of the corresponding sulfenamide, in which case no induction period is observed. If we assume a sulfenamide decomposition according to Reaction (a) so that Reactions (b) and (c) can proceed and crosslinking according to Reaction (d) is the necessary consequence then we

must ask which of these processes will account for the fact that the molecular network is again degraded, especially when sulfur is actually combined with the rubber. Evidently we must take into account that sulfur itself takes part in the decomposition of the sulfenamide, but in what way is still not clear. In reference to this we may weigh the observation that certainly only a very small portion of the sulfur is consumed in the beginning of the incubation period (see Figure 16). Anyway, we see that vulcanization under the influence of sulfenamides is not yet fully understood; but the kinetic data have shown just where organic chemical studies can be started to help in the clarification.

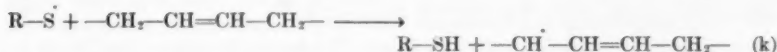
Also in vulcanizations where MBTS is used, we think of its homolytic decomposition, evidence for which has indeed been given by Dogadkin and coworkers⁴² as well as by us⁴⁵. We found—as already mentioned, in Section III, B, 5—that in the polymerization of Perbunan, induced by MBTS, the decrease in concentration of the initiator (MBTS) obeys a first order time law with a rate constant that is independent of concentration, which allows us to conclude that the decrease of MBTS is homolytic⁴⁵. Hence, in the first place if we consider $R-S-S-R$ as MBTS, we have



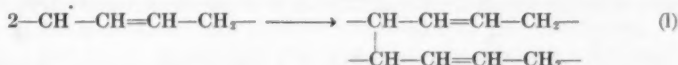
According to the experimental evidence we must assume that the radicals formed in Reaction (i) on the one hand induce polymerization at the vinyl side groups and on the other hand react with the α -methylene groups of the structural units, forming mercaptobenzothiazole and the already mentioned resonance stabilized polymer chain radicals which in turn combine in a crosslinking. So we have in addition:



and



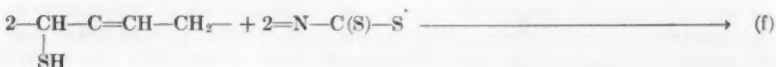
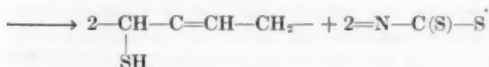
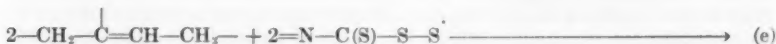
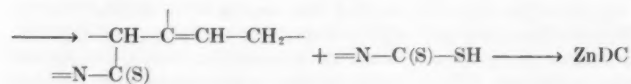
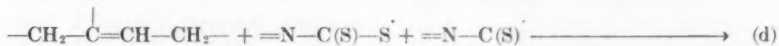
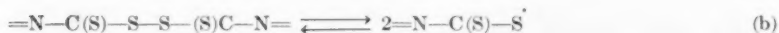
and

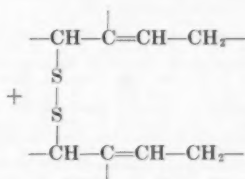
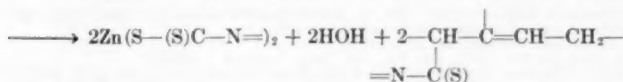
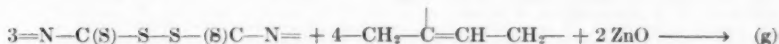
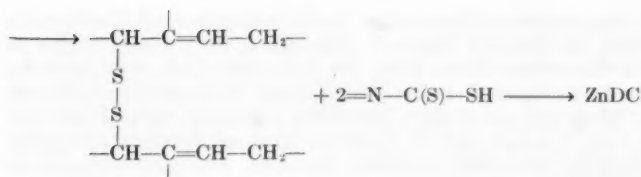


Because of the plausible hypothesis that the reactions formulated in (j), (k), and (l) really take place, we may expect, relative to the formation of MBT, that its kinetics will be in agreement with the information which is obtained from simultaneous reactions. Thus, it should obey a first order time law and its rate constant would have to be the same as for the MBTS decomposition. That is, the relations should be predominately analogous to those obtained in the vulcanization of natural rubber with dibenzoyl peroxide (Section III, D, 2). Here at least at lower temperatures, the benzoic acid (in our example corresponding to MBT) is formed at the same rate as that of the peroxide decomposition. While we found earlier that the rate constant for formation of MBT was always somewhat smaller than that for decrease in concentration of MBTS, we can say from the results of more recent investigations by Rucinski⁴⁶, in our Institute, who had substantially purer sample of NBR to work with, that the equality of the rates is quite well attained.

Up to now we get other relationships in the experiences with the vulcanization of natural rubber with MBTS (Section III, B, 5). The curves for the decrease of MBTS as well as those for the formation of MBT show an S-shape. Along the part of the curve which is convex to the time axis, the MBTS decrease does not follow a first order course, but the value of $n_t = 0.5$ is more often found there. The half-life times for MBT formation are always somewhat longer than those for the decrease of MBTS. We find yet other results for an MBTS-accelerated vulcanization of a sample of Perbunan which we know was not perfectly pure⁷⁸. There the MBT content in the vulcanizate runs through a maximum with the reaction time. The maximum shifts regularly with the temperature. This seems to us to mean that a reaction is proceeding here in which MBT that is once formed is being consumed again. Observations of this kind lead to the thought that the vulcanizations discussed here in detail are probably more complicated than the reaction schemes thus far postulated indicate.

Similarly for thiuram vulcanizations, whether it is by thiuram disulfide (TD) alone or a vulcanization with sulfur accelerated with TD. In view of all the quantitative data that are given, we cannot escape the impression, that all the mechanisms thus far proposed, plausible though they may be, leave many questions open, even though there is much probability for the partial reactions which are formulated in them. This statement is no criticism of those conceptions founded on experimental basis, which Craig and coworkers have developed, nor of the mechanism for thiuram vulcanization which was worked out by Bielstein⁷⁹ while working in our Institute, and which—while drawing upon several of the reactions postulated by Craig—for the first time substantiates the interpretation of our quantitative observations and leads us to the *overall reaction* given in (g)





Although Bevilacqua³⁰ finds the results of his investigations to be in agreement with this scheme, he feels that it does not include everything, and Moore³¹ comes to the conclusion that disulfide bridges, to which Bielstein's reaction sequence leads, are not very probable. In spite of such doubts (those brought up by Bevilacqua were considered in Section III, C, 2) it cannot be overlooked that the above reaction scheme explains the two-thirds transformation of TD to ZnDC and makes it comprehensible that thiuram fragments become combined with rubber (nitrogen content of the vulcanizate). It also indicates that ZnDC formation is necessary and must be connected with the crosslinking.

However that may be, the results of kinetic measurements raise a challenge to develop further ideas about the course of thiuram and other vulcanizations in specific reaction steps which will satisfy the kinetic findings; in our opinion, no easy task. At the present stage of the experimental results, the solution of our problem is chiefly an intellectual task. The reflections in which we are engaged would exceed the boundaries of this resumé; to discuss as far as possible the pertinent considerations would be premature at the time of the writing of this article.

The author is very much obliged to his coworkers for their excellent work. Without them it would have been impossible to assemble this extensive experimental material to present a survey of the prevailing kinetic relationships in vulcanization processes. He owes especial gratitude, however to his friend Director Dr. Walter Stegeman (Hamburg-Harburg) for his encouragement to stick to the task that was mapped out. Most hearty thanks are given to Professors Dr. Franz Patat (München) and Dr. Hermann Braune (Hannover) for many stimulating discussions.

The work was supported financially by the association of the German Rubber Industry, the German Research Association, the Federal Bureau of Economics, the Chemische Werke Hüls, the Bunawerk Hüls, the Hoechst Farbwerk, the Farbenfabriken Bayer, the Badische Anilin- und Soda-Fabrik, and Degussa. Moreover, the Phillips Petroleum Company, through the kind services of Dr. Gerard Kraus, and the Goodyear Tire and Rubber Co. supplied the Rubber Institute with newer synthetic rubbers. The author thanks all these agencies for the support which they have given these investigations.

V. REFERENCES

- ¹ Farmer, E. H., "Advances in Colloid Science", Vol. II, Interscience Publishers, Inc., New York, 1946, p. 229. (There are a number of references to pertinent work).
- ² Craig, D., RUBBER CHEM. AND TECHNOL. **30**, 1291 (1957).
- ³ Letort, M., *J. Chim. Phys.* **34**, 206 (1937); also *Bull. Soc. Chim. France* **9**, 1 (1942).
- ⁴ Compare Laidler, K. J., "Chemical Kinetics", McGraw-Hill Book Co., Inc., New York, 1950, p. 17.
- ⁵ Compare Frost, A. A. and Pearson, R. G., "Kinetics and Mechanism", John Wiley and Sons, Inc., New York, 1953, p. 15.
- ⁶ Spence, D. and Young, J., *Kolloid-Z* **11**, 28 (1912).
- ⁷ van Rossum, A., Comm. Netherland. Govt. Inst., Delft, 1917.
- ⁸ Twiss, D. F. and Brazier, S. A., *J. Soc. Chem. Ind.* **39**, 125 (1920).
- ⁹ Webster, R. M., RABRM, Research Paper No. 12, Croydon, 1923.
- ¹⁰ Park, R. C., *Ind. Eng. Chem.* **22**, 1004 (1930).
- ¹¹ Garvey, B. S. and White, W. D., *Ind. Eng. Chem.* **25**, 1042 (1933).
- ¹² Springer, A., *Monatsh. Chem.* **78**, 201 (1946). Contains other references.
- ¹³ Lewis, W. K., Squires, L., and Nutting, R. D., *Ind. Eng. Chem.* **29**, 1135 (1937).
- ¹⁴ Skellon, H., *J. Soc. Chem. Ind.* **34**, 671 (1915).
- ¹⁵ Nordlander, J., RUBBER CHEM. AND TECHNOL. **4**, 164 (1931).
- ¹⁶ van Iterson, G., *Kunststoffe* **10**, 133 and continuations (1917).
- ¹⁷ Compare, Echte, E., Scheele, W., and Sonnenberg, S., *Kautschuk u. Gummi* **12**, WT233 (1959); also unpublished research by Scheele, W. and Müller, H., as well as by Scheele, W., and Schulze, W.
- ¹⁸ Oldham, E. W., Baker, L. M. and Craytor, M. W., *Ind. Eng. Chem. Anal. Ed.* **8**, 419 (1936).
- ¹⁹ Scheele, W., and Ilachner-Gensch, Chr., *Kautschuk u. Gummi* **8**, WT55 (1955); also Birghan, K., Dissertation, Hannover, 1958.
- ²⁰ Gordon, M., *J. Polymer Sci.* **3**, 438 (1948) and RUBBER CHEM. AND TECHNOL. **25**, 1 (1952); also *J. Polymer Sci.* **7**, 485 (1951).
- ²¹ Studebaker, M. L., and Nabors, L. G., RUBBER CHEM. AND TECHNOL. **32**, 941 (1959).
- ²² Studebaker, M. L., *Kautschuk u. Gummi* **14**, WT177 (1961); also Reference 21.
- ²³ Moore, C. G., Unpublished work; Compare Bateman, L., Moore, C. G., and Porter, M., *J. Chem. Soc.* 2866 (1958).
- ²⁴ Bergem, N., cited by Craig, D., Reference 2.
- ²⁵ Kemp, A. R., Malm, F. S., and Stratielli, B., *Ind. Eng. Chem.* **36**, 109 (1944); See also Reference 2, p. 1310.
- ²⁶ Bateman, L., Moore, C. G., and Porter, M., *J. Chem. Soc.* 2866 (1958).
- ²⁷ Compare: Scheele, W., and Cherubim, M., *Kautschuk u. Gummi* **10**, WT285 (1957); Scheele, W., and Cherubim, M., *Verhandlungsb. Kolloid-Ges.* **18**, 115 (1958); Scheele, W., Toussaint, H. E., and Chai, Y. K., *Kautschuk u. Gummi* **12**, WT122 (1959); Scheele, W., *Rev. gen. caoutchouc* **36**, 1695 (1959); Scheele, W., and Redetzky, W., *Kautschuk u. Gummi* **12**, WT205 (1959); Scheele, W., and Cherubim, M., *Kautschuk u. Gummi* **13**, WT49 (1960); the section also contains unpublished results by Scheele, W., Kerrutt, G., Schapper, H., Müller, K. H., Helberg, J., and Teckkas, A.
- ²⁸ Laidler, K. J., "Chemical Kinetics", McGraw-Hill Book Co., Inc., New York, 1950, p. 275; and "The Chemical Kinetics of Enzyme Action", Clarendon Press, Oxford, 1958, p. 55.
- ²⁹ Michaelis, L., and Menten, L. M., *Biochem. Z.* **49**, 333 (1913).
- ³⁰ Briggs, G. E. and Haldane, J. B. S., *Biochem. J.* **19**, 338 (1925).
- ³¹ Krebs, H., *Angew. Chem.* **65**, 74 (1953); *Gummi u. Asbest* **8**, 68 (1955); "Die katalytische Aktivierung des Schwefels", No. 540 der Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, Köln u. Opladen, 1958; additional literature references there. Also, Schmidt, M., *Angew. Chem.* **61**, 394 (1961).
- ³² Laidler, K. J., Reference 28.
- ³³ Langenbeck, W., and Riehm, H. E., *Kautschuk* **12**, 156 (1936); Morris, R. E., *Ind. Eng. Chem.* **34**, 503 (1942); Lewis, W. K., Squires, L., and Nutting, R. D., Reference 13; Krebs, H., Reference 31.
- ³⁴ Krats, G. D., Young, H. H., and Katz, J., *Ind. Eng. Chem.* **41**, 399 (1949); Lewis, W. K., Squires, L., and Nutting, R. D., Reference 13.
- ³⁵ Compare Lorenz, O., and Echte, E., *Kautschuk u. Gummi* **10**, WT23 (1957); Lorenz, O., and Echte, E., *Verhandlungsb. Kolloid-Ges.* **18**, 142 (1958); Scheele, W., and Birghan, K., *Kautschuk u. Gummi* **10**, WT214 (1957); Scheele, W., and Schlüter, G., *Kautschuk u. Gummi* **13**, WT387 (1960).
- ³⁶ From investigations by Echte, E., and Scheele, W.
- ³⁷ van Alphen, J., *Angew. Chem.* **66**, 197 (1954).
- ³⁸ Birghan, K., Dissertation, Hannover, 1958.
- ³⁹ Lorenz, O., and Echte, E., *Kautschuk u. Gummi* **10**, WT81, WT273 (1957).
- ⁴⁰ Bergem, N., cited by Craig, D., Reference 2, p. 1311.
- ⁴¹ Gee, G., and Morell, S. H., RUBBER CHEM. AND TECHNOL. **25**, 454 (1952); Bielsstein, G., RUBBER CHEM. AND TECHNOL. **34**, 319 (1961).
- ⁴² Compare, e.g. Dogadkin, B. A., Selynkova, V., Tarasowa, Z., Dobromyslova, A., Feldshtein, M., and Kalpnov, M., RUBBER CHEM. AND TECHNOL. **29**, 917 (1956); Dogadkin, B. A., *Kautschuk u. Gummi* **12**, WT5 (1959); Dogadkin, B. A., Feldshtein, M., Dobromyslova, A., Shkurina, V., and Kalpnov, M., RUBBER CHEM. AND TECHNOL. **27**, 920 (1954).
- ⁴³ Scheele, W., and Müller, K. H., unpublished work.
- ⁴⁴ Cutforth, H. G., and Selwood, P. W., *J. Am. Chem. Soc.* **70**, 2785 (1948).

- ⁴⁸ Scheele, W., and Stemmer, H. D., *Kautschuk u. Gummi* 11, WT325 (1958); Stemmer, H. D., Dissertation, Hannover, 1959; contains literature references and unpublished work of J. Rucinaki.
- ⁴⁹ Tsurugi, J., and Fukuda, H., *RUBBER CHEM. AND TECHNOL.* 31, 779, 788, 800 (1958).
- ⁵⁰ Compare, Scheele, W., Toussaint, H. E., and Chai, Y. K., *Kautschuk u. Gummi* 12, WT122 (1959); unpublished work with Kerrutt, G. and Helberg, J.
- ⁵¹ Feldshtein, M. S., Eltingon, I. L., and Dogadkin, B. A., *RUBBER CHEM. AND TECHNOL.* 33, 357 (1960); for further work on the action of sulfenamides see Dogadkin, B. A., Beliatkaya, O. N., Dobromyslova, A. B., and Feldshtein, M. S., *RUBBER CHEM. AND TECHNOL.* 33, 361 (1960).
- ⁵² Scheele, W., and Schulze, W., unpublished work.
- ⁵³ Scheele, W., Lorenz, O., and Dummer, W., *Kautschuk u. Gummi* 7, WT2: WT27 (1955); Scheele, W., and Lorenz, O., *Ibid.* 8, WT85 (1955); Scheele, W., and Bielstein, G., *Kautschuk u. Gummi* 8, WT251 (1955); Scheele, W., and Stange, P., *Kautschuk u. Gummi* 9, WT110 (1956); Scheele, W., and Toussaint, H. E., *Kautschuk u. Gummi* 9, WT149; WT243 (1956); Bielstein, G., and Scheele, W., *Kolloid-Z.* 147, 154 (1956); Scheele, W., *Kolloid-Z.* 146, 14 (1956); Lorenz, O., Scheele, W., and Redetzky, W., *Kautschuk u. Gummi* 9, WT269 (1956); Scheele, W., and Toussaint, H. E., *Kautschuk u. Gummi* 10, 51 (1957); Scheele, W., Toussaint, H. E., and Stange, P., *Kautschuk u. Gummi* 10, 109 (1957); Scheele, W., Grasemann, H., and Mau, G., *Kautschuk u. Gummi* 10, 241 (1957); Scheele, W., Grasemann, H., Mau, G., and Stange, P., *Kautschuk u. Gummi* 11, WT23 (1958); Scheele, W., and Hummel, K., *Kautschuk u. Gummi* 11, 267 (1958); Scheele, W., *Kolloid-Z.* 169, 91 (1960); Scheele, W., Kemme, G., and Mau, G., *Kolloid-Z.* 161, 132 (1958); Scheele, W., and Hillmer, K. H., *Kautschuk u. Gummi* 12, WT1, (1959); Scheele, W., Mau, G., and Kemme, G., *Kautschuk u. Gummi* 12, WT33 (1959).
- ⁵⁴ Craig, D., Juve, A. E., and Davidson, W. L., *J. Polymer Sci.* 5, 709 (1950); 6, 1; 7; 13 (1951); Craig, D., Davidson, W. L., and Juve, A. E., *J. Polymer Sci.* 6, 177 (1951); Craig, D., Juve, A. E., Davidson, W. L., Semon, W. L., and Hay, D. C., *J. Polymer Sci.* 8, 321 (1952); Bevilacqua, E. M., *RUBBER CHEM. AND TECHNOL.* 32, 721 (1959); 31, 559 (1958).
- ⁵⁵ Craig, D., Juve, A. E., and Davidson, W. L., *J. Polymer Sci.* 5, 709 (1950). References here to older work.
- ⁵⁶ Farmer, E. H., and Michael, S. E., *J. Chem. Soc.* 516 (1942); Farmer, E. H., *Trans. Faraday Soc.* 38, 356 (1942); but compare Gee, G., *J. Polymer Sci.* 2, 451 (1947).
- ⁵⁷ Jarrison, A., *RUBBER CHEM. AND TECHNOL.* 19, 1061 (1946).
- ⁵⁸ Moore, C. G., *J. Polymer Sci.* 32, 503 (1958); also see Farmer, E. H., Ford, J. F., and Lyons, J. A., *J. Appl. Chem. (London)* 4, 554 (1954).
- ⁵⁹ Bruni, G., and Romani, E., *India Rubber J.* 60, 73 (1921) as well as Bruni, G., *India Rubber J.* 62, 89 (1921).
- ⁶⁰ Compare Scheele, W., and Gensch, Chr., *Kautschuk u. Gummi* 6, WT147 (1953); Hummel, K., and Bertram, H. H., *Kautschuk u. Gummi* 13, WT132 (1960).
- ⁶¹ Dunn, J. R., and Scanlan, J., *J. Appl. Polymer Sci.* 1, 84 (1959).
- ⁶² Dogadkin, B. A., Private communication; compare Dogadkin, B. A., and Sherahnev, V. A., *RUBBER CHEM. AND TECHNOL.* 33, 401 (1960).
- ⁶³ Unpublished work by Kemme, G., and Scheele, W.
- ⁶⁴ Hummel, K., Dissertation, Hannover, 1959.
- ⁶⁵ Compare Scheele, W., and Franck, A., *Kautschuk u. Gummi* 11, WT51 (1958); Scheele, W., Bertram H. H., and Hummel, K., *Kautschuk u. Gummi* 14, WT87 (1961).
- ⁶⁶ Maximow, A., *Caoutchouc, gutta-percha* 18, 1094 (1921).
- ⁶⁷ Perhaps these statements give an answer to the discussions on this subject in the work of Bevilacqua, E. M., *RUBBER CHEM. AND TECHNOL.* 31, 559 (1958); also Dunn, J. R., and Fogg, S. G., Reference 58.
- ⁶⁸ Compare, e.g., Brawden, M., Fletcher, W. P., and McSweeney, G. P., *Trans. Inst. Rubber Ind.* 30, 44 (1954); *RUBBER CHEM. AND TECHNOL.* 28, 190 (1955). Contains additional references.
- ⁶⁹ Compare Farmer, E. H., and Moore, C. G., *J. Chem. Soc.* 142 (1951).
- ⁷⁰ Brawden, M., Fletcher, W. P., and McSweeney, G. P., Reference 65.
- ⁷¹ Amberg, L. O., and Willis, W. D., *Proc. Intern. Rubber Conf.*, Washington, 1959, p. 565.
- ⁷² Parks, C. R., and Lorenz, O., *J. Polymer Sci.* 50, 287 (1961); See also *Kautschuk u. Gummi* 13, WT206 (1960).
- ⁷³ Hummel, K., Scheele, W., and Hillmer, K. H., *Kautschuk u. Gummi* 14, WT143 (1961).
- ⁷⁴ Kharasch, M. O., Forro, A., and Nudenberg, W., *J. Org. Chem.* 16, 105 (1951).
- ⁷⁵ Flory, P. J., and Rehner, J., *J. Chem. Phys.* 11, 251 (1943); Flory, P. J., "Principles of Polymer Chemistry", New York, 1953.
- ⁷⁶ van Rossem, A., Dekker, P., and Prawirdopoero, R. S., *Kautschuk u. Gummi* 7, 202 (1931); *RUBBER CHEM. AND TECHNOL.* 5, 97 (1932); Farmer, E. H., and Michael, S., *J. Chem. Soc.* 513 (1942); Farmer, E. H., and Sutton, A. D., *J. Chem. Soc.* 139 (1942); Brawden, M., Fletcher, W. P., and McSweeney, G. P., Reference 65.
- ⁷⁷ Bartlett, P. D., and Altshul, R., *J. Am. Chem. Soc.* 67, 812; 816 (1945).
- ⁷⁸ Lorenz, O., and Scheele, W., *Kautschuk u. Gummi* 8, WT273 (1955).
- ⁷⁹ Scheele, W., and Hillmer, K. H., not otherwise published.
- ⁸⁰ Martin, G. M., Roth, F. L., and Stiehler, R. D., *RUBBER CHEM. AND TECHNOL.* 30, 876 (1957).
- ⁸¹ Scheele, W., and Stemmer, H. D., not otherwise published.
- ⁸² Bielstein, G., and Scheele, W., *Kolloid-Z.* 147, 152 (1956).
- ⁸³ Bevilacqua, E. M., *J. Polymer Sci.* 28, 651 (1958).
- ⁸⁴ Moore, C. G., *J. Polymer Sci.* 32, 503 (1958).

OIL-EXTENDED RUBBERS

E. B. STOREY

RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LIMITED,
SARNIA, ONTARIO, CANADA

CONTENTS

	PAGE
I. Introduction.....	1403
II. Plasticization of rubber.....	1404
A. Natural rubber.....	1404
B. Synthetic rubber.....	1405
III. Extension principle.....	1407
A. Polymer contribution.....	1408
(a) Molecular constitution.....	1408
(b) Network structure.....	1410
(c) Blended compositions.....	1413
B. Extender contribution.....	1416
(a) Chemical characteristics.....	1417
(b) Physical characteristics.....	1423
(c) Blended compositions.....	1426
C. Pigment contribution.....	1429
Reinforcement.....	1429
D. Masterbatch design.....	1430
(a) Mode of blending.....	1433
(b) Tread-type masterbatch.....	1435
(c) Processing characteristics.....	1440
(d) Polymer-extender balance.....	1443
IV. SBR-masterbatched materials.....	1444
A. Manufacture.....	1444
(a) Processes.....	1445
(b) Inspection tests.....	1446
B. Commercial products.....	1447
(a) Composition.....	1447
(b) Polymer-extender materials.....	1448
(c) Polymer-extender-pigment materials.....	1450
(d) Special types.....	1450
Different polymeric materials.....	1450
Different extender materials.....	1450
V. Technology.....	1451
A. Compounding principles.....	1451
B. Manufacturing practices.....	1454
C. Vulcanizate characteristics.....	1455
D. Commercial applications.....	1460

VI. Other butadiene rubbers.....	1462
A. Alfin-catalyst polymers.....	1462
B. Ziegler-catalyst polymers.....	1464
C. Alkyl lithium catalyst polymers.....	1466
D. Acrylonitrile-butadiene copolymers.....	1466
VII. Neoprene types.....	1468
VIII. Butyl rubbers.....	1473
IX. Ethylene-propylene copolymers.....	1480
X. Summary.....	1483

I. INTRODUCTION

One of the first classes of compounding ingredients employed in the manufacture of rubber articles were the substances that became known as "softeners". These materials were liquid or semisolid products of natural origin that were mixed into the tough natural rubber to modify its elastic-plastic properties. They included various waxes, oils, pitches, tars, etc. The softener was not added simply for economical reasons. It conferred valuable technical properties by improving the ease of the mixing and shaping operations and modifying the physical characteristics of the composition. As the volume of rubber products increased during the first quarter of the twentieth century, larger volumes of softeners and rubber substitutes were employed to extend the available supplies of natural rubber imports and to adapt the physical characteristics of the products in line with the service requirements. The introduction of carbon black in 1912 increased the value of these processing aids in mixing operations and allowed the carbon black to be adequately dispersed in the rubber matrix without excessive mastication or breakdown of the natural rubber.

The first types of synthetic rubber¹ were tough materials that did not break down readily through mastication. DuPrene² was introduced in 1931 and it was the first high quality synthetic rubber of commercial importance to be amenable to the plasticizing and reinforcing practices applied to natural rubber. Technical and economical reasons dictated the use of mineral oils as softeners for DuPrene and its successor, neoprene. When Buna S polymers were first manufactured in Germany³, a shortage of petroleum oils encouraged the development of thermal methods of plasticization of the extremely tough, elastic product. At the start of the second world war, considerable quantities of petroleum pitches and tars were being employed to modify the properties of the Buna S rubbers.

The initial quantities of GR-S produced in the United States were of a highly elastic nature⁴ and immediate attention was directed towards finding suitable softening agents that would provide a sufficient improvement in processability to attain the necessary volume of quality rubber articles. Experiments were carried out at the Wilmington Chemical Corporation under the direction of Rostler⁵ to employ relatively large quantities of a "resinous fraction of petroleum" (called Naftolen)^{6, 7} as an extender to plasticize GR-S. This product had been developed originally in Austria⁸ and proposed as a processing aid for use with Buna S-3. Reports⁹ of this work to the Rubber Director's Office were made in 1942 but, at this stage in the synthetic rubber development, the properties of the GR-S product were not conducive to such an approach and, indeed, the technology was not prepared to associate satisfactory performance in service with a reduction in the rubber content of the article.

When low temperature polymerization systems were adopted to produce improved types of GR-S, however, attention was once more directed towards the use of petroleum products as extenders instead of merely softeners for the raw rubber compound. The successful development of the sulfoxylate activation system¹⁰ made it possible to produce higher molecular weight polymers and finally Rostler's goal was achieved by the announcement in 1951 of the first commercial oil-extended products; Polysar Krynol¹¹ in Canada and X-628¹² in the United States. Since that time, the value of the oil extension principle has become more fully understood and accepted. Oil-extended rubbers have played a vital role in establishing synthetic rubbers in a dominant position in North America and their attractive technical and economic advantages are at the forefront in the explosive establishment of synthetic rubber manufacturing facilities around the globe.

This review traces the development and adoption of the oil extension principle in the field of styrene-butadiene (SBR) copolymers and explores the literature relating to the application of such procedures to other synthetic rubbers. On the eve of the commercial introduction of stereospecific rubbers it is appropriate to consider the prospects for adapting such practices to these new polymers.

II. PLASTICIZATION OF RUBBER

One of the earliest reports on india rubber may be interpreted to state that Columbus noted that the natives employed materials such as animal grease to mix with the rubber latex in making play balls for their children. Natural rubber is a strong elastic material that may be more easily worked on mechanical mixing equipment after it has been subjected to an initial breakdown treatment by thermal or mechanical methods. It is not surprising that with the first, crude machines for masticating natural rubber recourse was made to additions of various natural products to soften the rubber. This process is a physical plasticization of the rubber and it is inherent in the nature of the operation that the physical strength of the vulcanized composition will not be increased, although a more useful balance of properties may result from its application. It is necessary to draw a distinction between the use of softeners primarily for plasticization and the use of such materials in the extension of SBR copolymers. In the later case, an extremely elastic polymer is combined with a relatively large quantity of a softener to provide a rubbery composition and, in a case of true extension, the physical strength of the vulcanized compound will be equal or higher than may be obtained without the use of the softener. The definition proposed by the ASTM Committee¹³ will be employed in this review to differentiate between these two cases. Where fourteen parts of a softener or less are employed per hundred parts of rubber the use is one to achieve plasticization (a process aid). If fifteen or more parts of softener are employed it is a case of extension of the rubber portion.

A. NATURAL RUBBER

Mention has already been made of the universal practice of adding softeners to natural rubber compositions¹⁴ to facilitate the plasticization of the raw rubber, improve the dispersion of fillers, and reduce the work, temperature and time expended in the mixing and shaping operations. Any standard list of commercial compounding ingredients for rubber provides a knowledge of the

host of materials that have been employed, not only to perform the functions mentioned above, but also to confer specific characteristics on the vulcanized compound. Among such properties may be mentioned those of hardness, modulus, low temperature flexibility, heat resistance, resistance to crack growth, etc.

The best-known softener for natural rubber is pine tar. It has been employed so widely in natural rubber articles that the general public believes that its characteristic aroma enables them to distinguish an article containing natural rubber from one containing a synthetic rubber. A standard reference on rubber compounding practices illustrates the general effect of a softener on the properties of a simple rubber compound. The vulcanizate is softer, more flexible and has a lower tensile strength.

The idea to incorporate the softener into the rubber in the latex stage is not a new one but has been practiced for many years in latex technology. The incorporation of large quantities of softeners to extend the natural rubber latex is the subject of several patents^{15, 16, 17} in the decade between 1925 and 1935. Marchionna¹⁸ reports many such instances where large quantities of softeners (ca. 40 to 50% by weight) were added to natural rubber latex as dispersions, or emulsions, and the whole was "co-coagulated" to provide a masterbatch. The principal objects of this process were to effect an economy in rubber use and to plasticize the rubber so that it was easier to work on mill rolls.

About the same time Wiegand¹⁹ described a method for incorporating carbon black into natural rubber in the latex stage. This is one of the first references to the present class of carbon black masterbatches employed for SBR rubbers.

The aim to produce a completely compounded natural rubber in the latex stage from which an automobile tire may be "poured" has engaged the imagination of many technologists. Natural rubber latex cannot be reinforced by fillers in the latex stage²⁰. However, the formation of softener-filler masterbatches by a latex process is economically attractive and the plasticized, premixed "co-coagulant" offers definite technical advantages by facilitating the mixing operation and reducing the time required on factory equipment.

B. SYNTHETIC RUBBER

In SBR latexes, fillers, and particularly carbon blacks, are capable of producing reinforcement²⁰ in contrast to the effect in natural rubber latex where their behavior is one of a diluent. In the case of softeners, Cumar resins²¹ are known to produce an enhanced tensile strength in SBR compounds containing light-colored fillers. One might suspect, then, that certain differences would exist in the behavior of SBR towards fillers and softeners which might provide a commercial or technical advantage. It was unlikely, however, that in the midst of a gigantic project to launch a synthetic rubber industry to supply the urgent need of a replacement for natural rubber that any immediate consideration could be given to novel means for extending this new material by adding large quantities of softener. Indeed, this expedient was being practiced to conserve the dwindling supplies of natural rubber with a consequent reduction in the specified minimum values governing the physical properties of the rubber article.

One of the first synthetic rubbers that showed similarities to natural rubber with respect to a high regularity in chain structure, ability to crystallize under high strains, and a high pure-gum tensile strength was the chloroprene polymer,

DuPrene². This novel chemical rubber was produced in 1931, and sold at a high price during the initial production period. DuPrene could be plasticized with pine tar but its development would have been facilitated if a more economical softening agent could have been found, preferably one which could be used in appreciable amounts. Extensive evaluations showed that Circo light process oil (Sun Oil Company) was an efficient softener. Catton²² gave data which illustrate that the effect of this oil in neoprene compounds is quite similar to that of other softeners in natural rubber. In retrospect we may ascribe this observation to be a general one pertaining to the effect of softeners in polymers having a chain structure, or composition, sufficiently regular to permit an ordered alignment to be formed under strain.

In the case of SBR, however, the structure was quite heterogeneous both from the point of the arrangement of the butadiene and styrene units in a polymer chain and as concerns the linearity of the individual chains. Indeed, it was found desirable to limit the degree of conversion of the monomers to polymer at 72% for SBR polymerized at 122° F in emulsion²³. Otherwise, even in the presence of sufficient modifying agent (alkyl mercaptan), branched and crosslinked chain structures were formed which produced a rubber that was very difficult to process on factory equipment. An immediate large-scale investigation of a suitable means to plasticize SBR was required to provide an acceptable degree of processability on existing factory equipment.

It was known that German Buna S²⁴ was plasticized by thermal means as well as by addition of softeners. This process was not favored for GR-S because of possible unfavorable oxidative crosslinking reactions that would result in a deterioration in dynamic properties and, indeed, the low tear strength and high flex crack-growth of GR-S were a matter of serious concern. In the United States, an early trend was towards the addition of adequate quantities of softener. It was found that pine tar exerted a retarding effect on the rate of cure and petroleum tars and asphalt types of softener were preferred in the first instance. Later, petroleum oils were found to provide a favorable balance of properties and their use increased during the first decade of GR-S production. A comprehensive account of the effects of various types of softener in GR-S compounds is provided by Merrick²⁵ and by Ludwig et al.^{26, 27}. Extensive trials of GR-S compounded with various softeners were carried out under the program initiated by the Office of Rubber Reserve and served to form a valuable basis for the later development of oil-extended rubber.

In the United Kingdom, the problem of plasticizing GR-S was approached by mastication at relatively low temperatures and by the addition of softeners²⁸, or natural rubber reclaim. An interesting approach was to soak thin sheets of GR-S in mineral oil²⁹ and avoid the preliminary breakdown of the polymer until it had been softened by absorbed oil. Since GR-S was not produced in England at this time, an extension of this principle to incorporate the oil at the latex stage was not feasible in that country.

Chemical plasticization of GR-S by hot milling in the presence of aryl mercaptans³⁰ was also practiced and still provides a useful means to promote the breakdown of SBR types. This method, however, only affects the initial processability of the polymer and does not consider the economy resulting from the addition of softeners. Indeed, the tendency for the early GR-S product to undergo oxidative crosslinking, made it advisable to process this chemically-plasticized material in a short period before such adverse effects became appreciable following the exposure to elevated temperatures.

III. EXTENSION PRINCIPLES

In this review the "extension principle" will be used to describe a combination of polymer and softener that are combined to form a product having a plasticity suitable for normal compounding operations and whose vulcanizate properties are maintained at a satisfactory level by a particular selection of components that complement each other to such an end result.

An excellent description of the early investigations is presented by Rostler⁹ beginning with attempts to extend natural rubber latex with petroleum products in the laboratories of the University of Vienna in 1932⁸ and in those of the

TABLE I
DATA OF AN EARLY EXPERIMENT*** IN EXTENDING SBR WITH NAFTOLEN MV

Compound No.	1	2	3	4	5	6	7	8
Buna S—Goodyear	100.	95.2	90.90	83.30	80.	74.	66.6	50.
Plasticizer-Extender*	—	4.8	9.10	16.70	20.	26.	33.4	50.
Stearic acid	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Zinc oxide	5.	5.	5.	5.	5.	5.	5.	5.
Benzothiazyl disulfide	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20
Diphenylguanidine	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
MPC black	45.	47.60	50.	54.20	56.	59.30	63.30	72.50
Sulfur	1.80	1.85	1.92	2.00	2.04	2.11	2.20	2.40
Optimum cure at 45#	65'	50'	50'	65'	65'	65'	80'	**
Specific gravity	1.145	1.160	1.170	1.185	1.195	1.210	1.225	**
Shore A hardness (30 sec)	60	59	60	62	64	65	65	**
(Aged 7 days Geer Oven)	66	67	68	69	70	71	75	**
Modulus at 300% (psi)	1530	1290	1190	1260	1160	1200	1150	**
Modulus at 500% (psi)	—	2880	2720	2700	2570	2490	2280	**
Tensile at break (psi)	2980	3160	3000	2830	2850	2520	2400	**
(Aged 7 days Geer Oven)	2480	2840	2420	2510	2510	2370	2240	**
Elongation at break (%)	470	530	530	510	540	500	510	**
(Aged 7 days Geer Oven)	350	420	350	390	390	400	400	**
Set at break (%)	11	14	17	19	24	27	36	**
Abrasion DuPont Abrader (cc loss per h.p. hr)	16	18	53	63	90	109	Smeared	**
Shore A hardness, block	58	60	60	61	62	63	—	**
Tear resistance (lb/in)								
Lengthwise	320	390	390	400	420	320	310	**
Crosswise	330	390	390	350	430	340	420	**
Luepke resilience—								
1st impact	59	53	57	63	49	46	43	**
4th impact	13	9	12	17	7	6	5	**
Tensile \times elongation $\times 10^{-4}$	140	167	159	144	154	126	122	

* Naftolen MV used.

** Too soft to mix.

*** Reference 9, Table VIII.

Austro-American Rubber Works, Semperit. These experiments were continued with samples of Buna S (SBR) and Buna N (NBR) latex produced in Germany. In 1942 Rostler continued these tests using GR-S latex produced by the Dewey and Almy Chemical Company, extending it with up to 25 parts of the Naftolen 510 produced by Wilmington Chemical Corporation. These first trials with American-manufactured GR-S^{31, 32} are the forerunner of oil-extended rubber and the extent of these tests is indicated by the data contained in Table I. It is interesting to observe that the aim was to soften a tough polymer to a normal plasticity level by addition of a petroleum product and to adjust the carbon black loading according to the combined quantity of extended product.

A. POLYMER CONTRIBUTION

Since the difficult-processing nature of early types of GR-S forced attention on the need for additions of softener, it is fitting that the polymer employed in oil-extended rubber should exert the major effect upon the polymer-softener combination. The peculiar nature of emulsion types of SBR copolymers⁴ allows them to exhibit the properties required for true extension to a remarkable degree. The development of this principle, then, will be confined to this product and the potential of other polymers will be explored in comparison with the styrene-butadiene emulsion system.

(a) *Molecular Constitution*

The GR-S emulsion polymerization in the United States was designed to produce a processable styrene-butadiene product having a bound styrene con-

TABLE II
POLYMERIZATION RECIPES

Recipe	(a) (Mutual)	(b) (Iron-pyrophosphate)	(c) (Sulfoxylate)
Polymerization temperature (° F)	122	41	41
Conversion (%)	72	60	60
<i>Monomers</i>			
Butadiene	75	72	71
Styrene	25	28	29
Water	180	180	200
<i>Emulsifier</i>			
Sodium fatty acid soap	5.0	—	—
Dresinate 731	—	5.0	—
Dresinate 214	—	—	4.5
<i>Electrolyte</i>			
Trisodium phosphate decahydrate	—	0.50	0.50
Sodium hydroxide	—	0.10	—
<i>Catalyst</i>			
Potassium persulfate	0.30	—	—
Cumene hydroperoxide	—	0.40	—
Paramenthane hydroperoxide	—	—	0.08
<i>Reducing Agent</i>			
Glucose	—	2.5	—
Sodium formaldehyde sulfoxylate	—	—	0.08
<i>Activator</i>			
Sodium pyrophosphate decahydrate	—	0.74	—
Ferrous sulfate heptahydrate	—	0.12	0.03
Sequestrene AA	—	—	0.035
<i>Modifier</i>			
<i>n</i> -dodecyl mercaptan	0.50	—	—
Mixed <i>tert.</i> mercaptan	—	0.20	0.18
Reference	125	35	10

TABLE III
MOLECULAR WEIGHT DISTRIBUTION OF SBR*

Number average molecular weight	Weight-%
less than 12,400	8.5
12,400	11.5
23,600	7.9
65,800	10.5
103,400	11.2
193,000	10.0
482,000	12.0
723,900	14.3
1,652,000	14.1

* Reference 36.

tent of 23.5%. The reaction was catalyzed by potassium persulphate and required some 16 to 20 hours at a temperature of 122° F. A typical recipe (Mutual) is given in Table II. A modifier, (dodecyl mercaptan) was employed to control the average molecular weight so that a processable polymer having a Mooney viscosity of 50 was produced at a conversion level of 72%. This conversion level was selected in order to restrict the degree of branching and crosslinking of polymer chains that became more pronounced at higher conversion levels through consumption of the modifier. The copolymer was completely soluble in toluene and had an average molecular weight of 150,000. The polymer was composed of chains of different molecular weight and a fractional precipitation technique was employed to provide the typical distribution data shown in Table III.

A factor introducing heterogeneity into the SBR, in addition to the random distribution of styrene and butadiene units along the polymer chain, is the manner in which two butadiene units may join together. Thus, the butadiene portion of the copolymer has been reported to contain the average structure composition given in Table IV. This composition varies in a predictable manner depending upon the polymerization temperature as reported by Meyer³³. It was found that SBR polymer formed at 41° F, the so-called "cold rubber", had a higher content of *trans* 1-4 butadiene units (Table IV) and a lower percentage of vinyl or 1,2 units. The improvements in the processing characteristics and physical properties reported for cold SBR³⁴ were facilitated by his increased uniformity in the structural composition. The major effects, however, are due to a reduction in the low molecular weight fraction and the ability to obtain a processable rubber at a higher average molecular weight.

The low temperature SBR polymerization was shortstopped at 60% conversion after initiation with an organic hydroperoxide, such as cumene hydroperoxide, and a "redox" activator. This activator combines a reduction-oxidation pair such as a ferrous salt and dextrose (Table II). Continued research on the polymerization system³⁵ allowed a reduction in the iron content

TABLE IV
STRUCTURE OF BUTADIENE UNITS IN SBR*

Polymerization temperature, ° F	122	41
1,2	22	18.5
<i>trans</i> 1,4	67	77

* Reference 33.

of the recipe, elimination of sugar in the activator, and finally to the introduction of the "sulfoxylate" recipe¹⁰ in which the iron activator is bound in a chelate complex with ethylenediamine tetraacetic acid from which it is liberated at a controlled rate to activate the polymerization. The low temperature SBR had a higher average molecular weight²³ than the copolymer produced at 122° F.

Yanko²⁶ obtained nine molecular weight fractions from GR-S by the precipitation technique and measured the properties of each fraction. He concluded that the stress-strain properties and quality index data vary directly with the number-average molecular weight of the polymer but that the processing characteristics became poorer at higher molecular weights. Kemp²³, Yanko²⁶ and Mark²⁷ report that GR-S polymerized at 122° F contains 30% or more of polymer having a molecular weight of 30,000 or less. While this low molecular weight fraction serves an essential purpose in rendering the high molecular weight fractions processible in factory equipment, it contributes very little to the strength of the vulcanized polymer.

The German Buna S-3 had a high average molecular weight and required a thermal depolymerization procedure in order to produce chain scission and reduce the molecular weight to a level suitable for compounding on factory equipment. The degree of scission could be controlled by the extent of the heat treatment to produce a polymer having the desired level of plasticity. The GR-S product could be prepared to a high molecular weight by reducing the quantity of modifier employed during polymerization. In either case, however, a relatively high percentage of low molecular weight material was required to allow the product to be handled on normal factory equipment.

(b) Network Structure

When the unsaturated units in the SBR polymer are crosslinked by heating in the presence of sulfur a continuous network is formed that converts the plastic rubber to an elastic material. The polymer is bound into the network by the crosslinks formed along the chains but a certain end portion of the long molecule remains free and presents a point of low strength in the network.

Similarly if diluent is present, either as low molecular weight polymer or as ingredients added prior to vulcanization, it will not contribute to the support of stress. Einhorn and McLeod²⁸ have developed an expression for the strength of a vulcanized diluent-polymer system which is outlined below.

Flory²⁹ has extended the classical theories of Guth and Mark, Kuhn and Wall, to include the effect of initial molecular weight on the relation of equilibrium stress, τ , to strain, α . His stress strain equation is:

$$\tau = \frac{RT\gamma g}{V} \left(1 - \frac{2M_c}{M}\right) \left(\alpha - \frac{1}{\alpha^2}\right) \dots \dots \dots (A)$$

where R = molar gas constant, T = absolute temperature, γ = number of polymer chains in volume V (cc.), g = a correction factor for chain entanglements, M = number average molecular weight of the polymer, and M_c = number average molecular weight between crosslinks.

The fraction $2M_c/M$ represents the portion of the elastomer which is in chain ends and which does not contribute to the support of stress by the network. If diluent is present, γ chains will be contained in a larger volume $V_1 = V/v_2$, where v_2 is the volume fraction of rubber in the rubber-diluent

system. Inserting $1 - v_1$ (v_1 = volume fraction of diluent) in place of v_2 in this expression, substituting the resulting value V_1 in Equation (A) and replacing γ/V by ρ/M_c , leads to (B):

$$\tau = \frac{RT\rho}{M_c} g \left(1 - \frac{2M_c v_2}{M} - v_1 \right) \left(\alpha - \frac{1}{\alpha 2} \right) \dots \dots \dots (B)$$

where ρ is the density of the polymer.

Flory²⁹ has demonstrated that Equation (B) explains the molecular weight dependence of τ for butyl rubber gum vulcanizates. His data for butyl rubber vulcanizates compounded with carbon black indicate that the term in the first bracket of Equation (B) satisfactorily explains the molecular weight dependence of the stress-strain properties and the tensile strength of these vulcanizates. This should also be true for any other rubber in which carbon black acts merely as a diluent with respect to stress-strain properties.

It is well known that the properties of gum vulcanizates of SBR type polymers have little dependence on molecular weight and that carbon blacks greatly increase the tensile strength and the modulus. Experience has shown that maximum reinforcement is achieved when the carbon black loading is 50 parts by weight per hundred parts of rubber (phr) plus extender. Results showed that, if this condition of maximum reinforcement is satisfied, the term in the first bracket of Equation (B) adequately explains the molecular weight dependence of both τ and the tensile strength for polymers of the SBR type.

By assuming adequate compensation for the presence of branched polymer chains and intramolecular crosslinks, Equation (B) was rewritten as:

$$\tau = E \left(1 - \frac{2M_c v_2}{M} - v_1 \right) \dots \dots \dots (C)$$

where τ is the tension at any specific elongation, α , and E is a constant dependent on R , T , ρ , g , M_c , and α . If the molecular weight of the polymer is changed to be a value M' it is necessary to change v_1 to v_1' if τ is to be maintained constant. Substitution of these values in Equation (C) gives:

$$v_1' = v_1 \frac{(1 - 2M_c/M)}{(1 - 2M_c/M')} + \frac{2M_c(1/M - 1/M')}{1 - 2M_c/M'} \dots \dots \dots (D)$$

By means of Equation (D) one may calculate the volume fraction of diluent v_1' permitted in a polymer of molecular weight M' in order to yield a vulcanizate having the same stress-strain relation and the same tensile strength as "reference" or "standard" polymer of molecular weight M associated with a volume fraction of diluent, v_1 . Einhorn and McLeod refer to v_1' as the permissible volume fraction of diluent which they define as either low molecular weight polymer or any nonpolymer ingredients added prior to vulcanization. They transformed Equation (D) into a more practical expression:

$$X_\tau = \frac{100v_1'}{1 - v_1'}$$

where X_τ = cc of diluent per 100 cc of rubber.

Given a value for M_c in Equation (D), it is possible to plot a curve of v_1' versus M' for any values of M and v_1 . A value of 30,000 was selected for M_c

based on work reported by Yanko³⁶. For crystallizing, non-SBR type polymers, it is possible to use any value of v_1 . However, for SBR types we must impose a lower limit corresponding to the volume fraction of additives required for maximum reinforcement.

Einhorn and McLeod selected SBR as the reference polymer and, since 30% of SBR is nonvulcanizable in a standard tread vulcanizate recipe³⁶, this amount of rubber must be considered as diluent in addition to the usual compounding ingredients. Figure 1³⁸ shows the calculated relationship for the permissible diluent concentration in any polymer of molecular weight M' which gives a system having the tensile properties of SBR ($M = 150,000$). This figure shows a second curve, corresponding to a rubber of molecular weight 250,000 compounded to maximum reinforcement, which demonstrates an important conclusion to be derived from this study, viz., there is little economic advantage in producing molecular weights above 500,000 if it is desired to match the properties of any standard equivalent to or better than SBR. Beyond this value of M' an infinite increase in molecular weight may be compensated for by a relatively small increment of diluent. This result explains

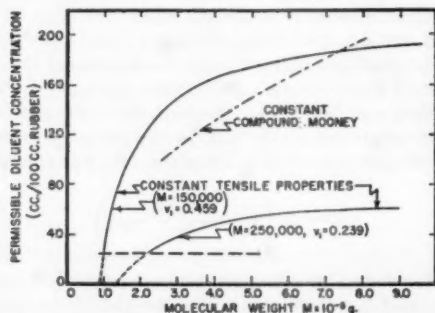


FIG. 1.—Theoretical effect of molecular weight of polymer on the diluent loading for constant tensile properties or constant compound Mooney viscosity. (Reference 38, Fig. 1.)

the observation⁴⁰ that alfin-catalyzed styrene-butadiene copolymers, whose molecular weights are of the order of 1,500,000 will tolerate only marginally more oil than similar polymers of molecular weight 300,000 at equivalent stress-strain properties. It is also interesting to note that as the standard of tensile strength is raised, the amount of permissible diluent will decrease rapidly.

Swart⁴¹ has shown that in compounds in which the ratio of carbon black to polymer plus oil is maintained constant, the concentration of diluent required to maintain a constant value for the compound Mooney viscosity increased linearly with the intrinsic viscosity of the initial polymer. Assuming a viscosity-molecular weight dependence of the same form as the modified Staudinger relation, led to an approximate relation:

$$X_p = x + yM^a \dots \dots \dots (E)$$

where X_p is the level of diluent required for constant Mooney viscosity (taken to indicate the degree of processability), x and y are empirical constants and a is always less than unity. This equation is useful if its application is restricted to molecular weights in the range where commercial polymers with essentially

no unvulcanizable rubber can be produced and to a single diluent type³⁸. The dotted line in Figure 1 is a hypothetical curve representing the concentration of diluent, as a function of molecular weight, to maintain a constant Mooney viscosity of 53.5 and it was estimated from data for 41° F styrene-butadiene copolymers compounded with different amounts of naphthenic-type oil and a constant loading of EPC carbon black based on the weight of polymer plus oil. The point of intersection of the constant Mooney viscosity and constant tensile strength curves represents the only value of M' consistent with the properties of the adopted standard, SBR.

This theory together with previous investigations³⁶ suggests that the low molecular weight material does not contribute to the strength of the network but only to the processibility of the product and, hence, it should be possible to substitute other compatible materials for the low molecular weight polymer and achieve similar results.

The effect of reducing the modifier level on the average molecular weight of the polymer was illustrated by Buckler and Mitchell⁴² by measuring the intrinsic viscosity^{43, 44} of the polymer for various levels of conversion (Figure 2). As the mercaptan is reduced from the normal level of 0.20 to 0.30 parts per

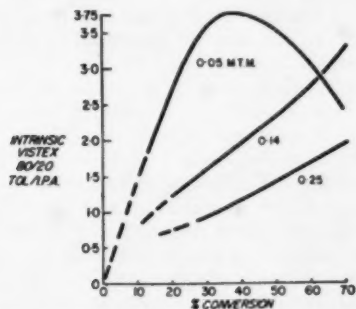


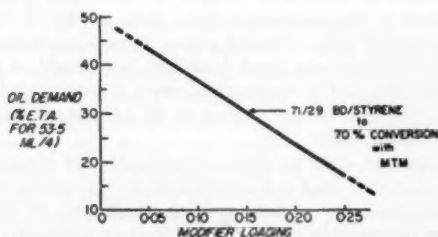
Fig. 2.—Effect of modifier loading on the viscosity-conversion relationship. (Reference 42, Fig. 3.)

hundred of monomer employed in the standard cold rubber recipe, the average molecular weight of the polymer at a fixed conversion level increases. However, there is a minimum level of modifier that must be present to exclude the formation of a crosslinked or "gelled" fraction. The formation of this gelled fraction is indicated in Figure 2 by the maximum in the curve at a level of 0.05 parts of MTM (mixed tertiary mercaptans) and, in this instance, the gelled fraction became apparent at a conversion of about 35%. The presence of this gelled fraction is detrimental to the processing and physical properties of the product and, hence, it is desirable to employ a level of modifier which will prevent the formation of gel up to the maximum conversion level encountered in the polymerization. A practical and economical conversion level has been found to be about 60% and, therefore, a normal modifier level for a high molecular weight polymer would be in the range of 0.10 to 0.16 in this case.

(c) Blended Compositions

The average molecular weight of SBR is normally estimated by a Mooney viscosity value determined⁴⁵ at 212° F. In general, a Mooney viscosity of

Fig. 3.—Effect of modifier charge on the oil demand of the polymer.
(Reference 42, Fig. 4.)



45 to 60 indicates a suitable plasticity for a styrene-butadiene copolymer. The higher average molecular weight polymers have a Mooney viscosity above 100 and there is some doubt about the accuracy of the measurement⁴⁵ because it is known that crumbling or "shearing" of the polymer may occur in the Mooney machine for such tough polymers. Difficulty has been reported⁴⁴ in estimating the average molecular weight by solution methods because the very long polymer chains do not readily untangle one from the other even at low concentrations and a standing time of uncertain length may be required to attain a solution suitable for an intrinsic viscosity measurement. These problems in estimating the molecular weight of the polymer have been resolved by blending with various amounts of a particular softener after which an accurate measure of the Mooney viscosity is possible¹¹. By extrapolating the Mooney viscosity versus softener loading relationship to zero softener one may arrive at a so-called "computed" Mooney value for the polymer. The method of blending the softener and polymer must be carefully regulated and preference is expressed for blending in the latex stage followed by coagulation and a careful drying schedule¹¹. A simple extraction technique using the ethanol-toluene azeotrope (ETA) (70% ethanol) has been devised to determine the softener level and it has the advantage that nonpolymer constituents such as residual soap and fatty acid are also extracted together with any soluble, very low molecular weight polymer that is present in the rubber. These latter materials were found to exert a softening effect upon the polymer hydrocarbon and are reported to be present in a high molecular weight SBR to the extent of about 7%. The expression *oil demand* has been employed by Buckler and Mitchell⁴² to indicate the amount of ETA—extractable material in a polymer-softener blend which has a Mooney value of 53.5 (ML/4', 212° F).

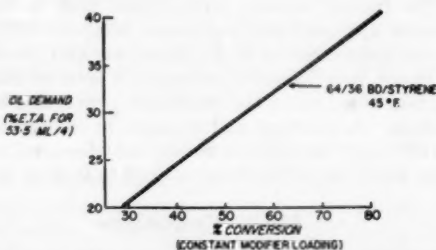


Fig. 4.—Effect of monomer conversion on the oil demand of the polymer.
(Reference 42, Fig. 5.)

They⁴² gave data that showed the effect of various modifier loadings at a constant conversion level (Figure 3) on the oil demand and for various conversions at constant modifier loading (Figure 4). These relationships show that the oil demand, a measure of the average molecular weight of the polymer, is linearly related to the modifier loading and the conversion level in the absence of gelled polymer.

A similar method of estimating the "computed" Mooney viscosity of the high molecular weight polymer is given by Swart⁴¹. Other data obtained by Stewart⁴⁰ have indicated that the Mooney value of a rubber may be estimated more properly by a linear extrapolation of the Mooney viscosity of the polymer-softener blend plotted against the percentage of rubber in the blend.

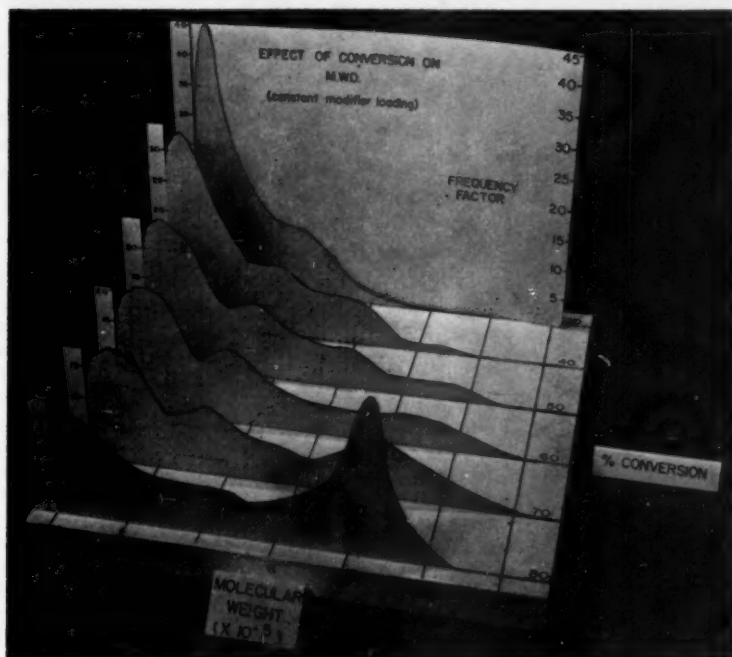


FIG. 5.—Variation of molecular weight distribution with conversion level at constant modifier charge (Reference 42, Figure 13).

Buckler and Mitchell⁴² estimated the molecular weight distribution of styrene/butadiene polymers by fractionation techniques to demonstrate further effects of conversion level at constant modifier loading (Figure 5). They reported that the range in molecular weight increases at higher conversions and that an increasing amount of polymer having an average molecular weight around 800,000 is formed at conversions over 50%. This fraction is believed to be formed through the reinitiation of lower molecular weight chains and subsequent polymerization to form branched chains. Other data are provided to show the relationship between molecular weight distribution and oil demand

at 60% conversion (Figure 6). The width of the distribution was observed to vary from 950,000 to approximately 1,200,000 as the oil demand varies from 25% to 45%. In addition, a high molecular weight peak, apparent at low oil demands in the 600,000 mol. wt. region, shifts to higher molecular weights and includes a larger proportion of the polymer. The presence of this high molecular weight peak is said to lead to less-desirable processing characteristics and, hence, should be avoided. This suggests that not only gelled polymer but even long chains, either branched or simply entangled one with another, are undesirable even in an extended rubber under certain operations involving high shear rates or short deformation times.

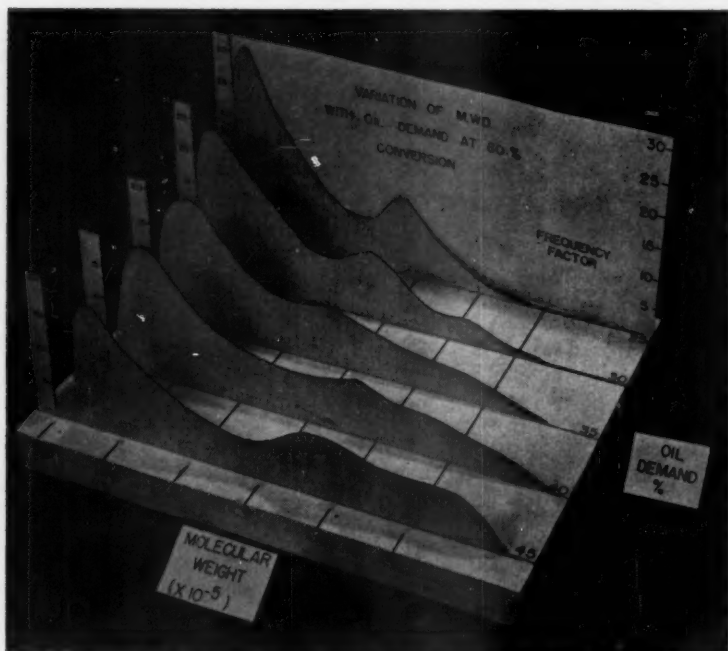


FIG. 6.—Variation of molecular weight distribution with oil demand of base polymer at 60% conversion (Reference 42, Figure 14).

B. EXTENDER CONTRIBUTION

The chemical and physical characteristics of the extender exert significant effects upon all the properties of the raw, compounded and vulcanized SBR masterbatch. A large number of references are available in the literature that ascribe special characteristics to various specific types of softener and demonstrate these effects by comparisons based upon equal weight loadings of the softeners concerned. Hundreds of various softener materials have been examined in SBR compounds^{26, 27} at loadings of 5 to 20 parts simply as processing aids, dispersants, tackifiers, protective waxes, elasticators, etc., so that the basic effects of many classes of such substances is well understood by the rubber

compounder. These same significant effects should be expected to be achieved by the use of a particular softener in a high molecular weight SBR polymer. A higher percentage of softener is present in the extended product than is employed in a standard SBR compound and it now becomes essential that the softener content be considered on a volume basis. The effects of molecular weight and the shape of the softener molecule become more significant at higher volume ratios. The average softener has a molecular weight in the range of 250 to 500 and, in essence, it extends the molecular weight range of the polymer by contributing a peak to the distribution in a region below that normally present in the cold SBR polymer. In addition, many commercial softeners contain high percentages of branched chains, condensed ring structures or a combination of these two types. These molecules differ from the short chains of styrene/butadiene copolymer in their ratio of effective length to cross-sectional area, effective volume, and in the lower number of configurations available to the molecule. In short, a number of thread-like chains have been replaced by a larger number of globular or octopus-like molecules. A major effect should be expected on the rheological properties of the raw and compounded SBR polymer. Relatively little work of this nature is reported in the literature.

(a) *Chemical Characteristics*

The chemical compounds⁴⁶ present in a petroleum oil are so varied and complex as to defy any attempt to isolate and identify more than a few of the more frequent and simple chemical compounds. Rather, the trend has been to classify various chemical groups of materials either on a basis of their solubility and chemical reactivity as favored by Rostler^{45, 47} or by a carbon-type analysis employing a silica gel procedure as proposed by Kurtz^{48, 49} (Table V). Both schools of thought have a number of supporters and both methods appear to provide a workable basis for classification of oil extenders. The difficult problem of resolving these two approaches into a compromise system, acceptable to both schools of thought, has been referred to the American Society for Testing Materials, Committee D-11.

It is generally recognized that petroleum hydrocarbons contain molecules that combine saturated paraffin-type chains, saturated ring systems, aromatic ring systems and heterogeneous compounds containing elements such as oxygen, nitrogen, sulfur, phosphorous, etc., in addition to carbon and hydrogen. This leads to a classification adopted by the Office of Rubber Reserve: paraffinic oils—predominantly straight chain, naphthenic oils—predominantly saturated cyclic compounds, aromatic oils—predominantly aromatic rings. The nitrogen-containing compounds, so-called nitrogen bases, do not find a place in this classification system but are contained in the larger amounts in the aromatic-type oils. Rostler⁴¹ and other workers in this field have shown that these nitrogen-containing compounds have an activating effect upon the vulcanization reaction. The asphaltene materials that contain a higher proportion of such nitrogen bases do not find extensive use as extender materials. The nitrogen bases need not be considered a critical component since they are present to a lesser or greater degree in the three classes of extender oil, depending upon the aromaticity of the oil. In this connection, it should be realized that only compounds containing aliphatic-type unsaturation can be crosslinked by sulfur-vulcanizing reactions and, hence, can offer any possibility for "co-vulcanization" with the polymer to form a single crosslinked network. The presence of

TABLE V
CHEMICAL COMPOSITION OF REPRESENTATIVE TYPES OF OIL*

	Relatively aromatic		Relatively naphthenic		Relatively paraffinic		
	A1	A2	S1	S2	S3	S4	S5
Molecular type analysis							
Aromatic hydrocarbons ^a , wt %	88.2	77.5	9.7	15.7	12.1	14.4	19.6
Naphthenic hydrocarbons, wt %	11.8	21.1	90.2	84.1	82.5	85.5	80.4
<i>n</i> -Paraffinic hydrocarbons, wt %	0.0	1.4	0.1	0.2	1.0	0.1	0.0
Average aromatic molecule							
R_A	2.1	2.7	1.3	1.4	1.2	1.3	1.2
R_N	1.3	1.6	1.9	2.5	1.7	1.7	2.8
C_P	4	11	12	14	12	16	35
Average saturated molecule							
R_N	3.2	3.3	2.7	3.6	1.7	2.0	2.9
C_P	10	21	13	18	17	20	34
Carbon type analysis							
C_A , %	46	33	3	4	3	3	2
C_N , % from aromatic molecules	23	16	3	5	4	3	4
C_P , % from aromatic molecules	19	28	4	7	6	8	13
C_N , % from saturated molecules	7	10	44	40	30	30	24
C_P , % from saturated molecules	5	13	46	44	57	56	57
Acid extraction							
% Extracted by 85% H ₂ SO ₄	5.4	10.8	negligible				
Nonhydrocarbon molecule							
Sulfur compounds ^b , max. %	4.7	8.3	8.8	0.9	0.7	1.0	0.7
Nitrogen compounds max. %	1.5	6.3	<0.02	<0.03	0.05	0.06	0.2
Oxygen compounds max. %	12.8	13.6	0.00	1.2	1.5	1.3	0.9

* Includes the nonhydrocarbons, which are neglected in calculating composition of average aromatic molecule.

^b Calculated using average molecular weight of the sample and assuming only one S, N, or O atom per molecule.

^c Reference 62, Table II.

aliphatic-type unsaturation is extremely unlikely in a petroleum oil fraction suitable for use as an extender and, hence, the extender oil is not chemically combined into the polymer network during vulcanization.

The normal refining operations remove any paraffin wax from the petroleum fractions that are supplied as extender oils. Thus, paraffinic hydrocarbons as such are not present in an extender and there is no likelihood that waxy blooms will form on the surface of compounds and interfere with lamination operations.

The predominant chemical effect of the extender oil is the degree of compatibility with the polymer hydrocarbon. This depends, primarily, upon the similarity in the cohesive energy density values for the extender and the polymer. A simple method of determining the compatibility is to measure the swelling of the unvulcanized polymer in the oil^{60, 61}. In general, saturated hydrocarbons have a limited degree of compatibility with most rubbers, including SBR. Since the saturated units are mainly present as side chains on ring structures, the degree of incompatibility encountered is such that the paraffinic-type oils show a certain lubricating effect and, in the extreme may "bloom" or show a surface excess of one or more of the more saturated, straight-

chain components. The aromatic oils are the more compatible types and they show a definite tendency to exert a "solvent" action on the polymer so that the masterbatch containing these oils is likely to exhibit some degree of surface tack and a higher flow at elevated temperatures. The naphthenic types occupy an intermediate position in these respects.

One characteristic that has required considerable attention has been the tendency for some oil-extended rubbers to become plasticized during the drying operation or during storage of the product. Quite considerable decreases in Mooney viscosity⁵² have been reported to occur in some instances and these appear to be most frequently associated with use of a highly-aromatic oil. Extensive evaluations were reported by Taft and co-workers^{53, 54, 55} on this phenomenon and he favored an oxidation effect promoted by nitrogen-base components in the relatively-aromatic oils.

The "heat softening" of oil extended rubbers was not a consistent phenomenon but, periodically, severe breakdown would be encountered either in the production unit or in Pilot Plant operations. Mitchell⁵⁶ showed that "heat softening" could be promoted by the addition of trace amounts of heavy metals to the salt-acid coagulant (Table VII). A significant decrease in either the Mooney viscosity of the masterbatch, or the intrinsic viscosity of the base polymer, was produced by heating in air at 150° F and the extent of the effect varied with the type and quantity of heavy metal added in the coagulant. Iron is a likely contaminant that may be derived from the manufacturing equipment or the process chemicals. Mitchell (Table VIII) showed that the intrinsic

TABLE VI
PHYSICAL PROPERTIES OF REPRESENTATIVE TYPES OF OIL*

	Relatively aromatic		Relatively naphthenic		Relatively paraffinic		
	A1	A2	S1	S2	S3	S4	S5
Inspection data							
Gravity, ° API at 60° F	9.1	11.8	27.2	23.3	32.0	30.4	28.0
Aniline point, ° F	27	133	199.2	220.8	207.7	222.1	271.4
Pour point, ° F	5	55	-25	5	5	0	0
Flash point, ° F	340	475	335	455	360	440	590
Fire point, ° F	390	550	380	520	415	490	635
NPA color	>8	>8	3½	5½	1	1½	5
Vacuum Engler, 10 mm							
IBP	228	467	296	485	306	465	565
10%	376	547	397	537	418	492	685
50%	428	593	446	558	459	519	722
90%	506	660	510	614	492	557	—
98%	549	700	545	640	523	581	—
Carbon, %	88.9	87.5	86.4	86.6	86.1	86.2	86.2
Hydrogen, %	9.65	10.9	13.4	13.3	13.7	13.7	13.8
Sulfur, %	0.55	0.62	0.07	0.06	0.06	0.08	0.03
Nitrogen, %	0.075	0.206	<.001	<.001	0.002	0.002	0.003
Oxygen, %	0.75	0.51	0.00	0.04	0.07	0.05	0.02
Other physical properties							
d ₄ ²⁰	1.0026	0.9837	0.8879	0.9105	0.8615	0.8704	0.8835
n _D ²⁰	1.5737	1.5550	1.4847	1.4971	1.4748	1.4793	1.4865
Specific dispersion ^a	212.5	188.5	102.2	104.3	104.2	103.6	104.2
n - d ₄ ²⁰	1.0724	1.0631	1.0407	1.0419	1.0440	1.0441	1.0448
Vis. 100°, centistokes	73.5	3130	32.3	273	20.5	45.7	490
Vis. 210°, centistokes	5.30	38.0	4.73	15.2	3.90	6.35	30.6
Vis. 100°, Saybolt seconds	340	14,500	151	1260	99.6	212	2260
Vis. 210°, Saybolt seconds	43.6	178	41.7	78.5	39.1	47.0	144
Viscosity index	-165	-119	50	37	88	94	98
Viscosity gravity constant	0.982	0.927	0.846	0.842	0.818	0.815	0.798
Molecular weight	272	427	347	464	352	419	698
Molecular volume	271	434	391	510	409	481	790

$$^a \text{ Specific dispersion} = \frac{n_D^{20} - n_C^{20}}{d_4^{20}} \times 10^4.$$

* Reference 62, Table I.

TABLE VII

DEGRADATION AT 150° F OF OIL-EXTENDED RUBBER (45 PARTS OF SUNDEX 53;
1.25 PARTS OF BLE) WITH VARIOUS HEAVY METALS
ADDED IN THE COAGULANT*

Metal	% ETA extract	Test	Time at 150° F, hours				
			1.75	6.5	10	15	25
Tin	29.5 ^a	ML/4'	—	64.0	64.5	62.5	64.0
		[η]	2.86	2.96	—	—	2.86
Zinc	36.2	ML/4'	54.0	56.0	57.5	57.0	57.5
		[η]	2.70	2.82	—	—	2.73
Nickel	36.7	ML/4'	50.5	56.0	—	55.5	53.0
		[η]	2.82	—	2.92	—	2.56
Chromium	36.0	ML/4'	55.0	50.5	50.0	45.0	37.5
		[η]	3.32	2.70	—	—	2.27
Cobalt	21.3 ^a	ML/4'	63.0	87.0	83.5	73.0	45.5
		[η]	2.99	—	2.83	—	2.02
Iron	36.7	ML/4'	44.0	47.5	42.5	39.0	32.5
		[η]	2.63	2.54	—	—	1.82
Manganese	36.5	ML/4'	56.0	40.0	30.0	10.0	—
		[η]	3.10	2.33	2.22	1.48	—
Copper	36.3	ML/4'	—	38.5	18.0	—	—
		[η]	2.60	1.64	1.48	1.11	—

* Reference 56, Table V.

viscosity varied inversely with the amount of added ferrous sulphate when the oil extended rubber was heated in air at 150° F although only a small effect was produced by drying the same masterbatches in vacuo.

These tests employed a relatively-aromatic extender oil and other work (Table IX) indicated that the "heat softening" was reduced when either a relatively-naphthenic oil or an ester-type plasticizer was present in the masterbatch. As might be expected, a staining-type stabilizer (BLE) afforded better protection under such conditions than a nonstaining type (Polygard).

TABLE VIII

EFFECT OF ADDED FERROUS SULFATE ON RETENTION OF
BASE POLYMER VISCOSITY*
(45 parts Sundrex 53, 1.25 parts BLE)

FeSO ₄ · 7H ₂ O added part	No. of runs	Vacuum dried	Hours at 150° F				
			3.5	6.5	10	15	25
Nil	3	92.9	94.0	94.6	—	92.9	87.2
0.005	1	92.8	96.0	97.3	—	93.9	89.8
0.010	3	95.6	96.2	93.8	—	87.1	72.5
0.025	1	92.8	89.6	86.9	—	74.6	61.8
0.050	2	93.9	86.8	85.8	—	73.6	61.5
0.080	1	—	85.8	82.3	—	—	59.0
0.100	2	94.0	89.7	87.5	—	72.1	69.2
0.250	3	97.4	91.7	87.2	—	75.7	66.5

	K ₂ P ₂ O ₇	Vacuum dried	Hours at 150° F			
			3.5	6.5	15	25
0.050	Nil	94.4	84.7	83.7	73.6	62.0
0.050	0.064	93.4	88.9	87.8	73.5	60.9
0.100	Nil	—	86.7	85.1	70.0	68.6
0.100	0.127	94.0	92.0	89.9	74.2	69.8

* Reference 56, Table VI.

Reynolds⁵⁷ confirmed this effect of trace heavy metals and showed that the chemical nature of the oil was a contributing factor (Figure 7). Thus, a masterbatch containing a naphthenic oil showed about the same reduction in Mooney viscosity or dilute solution viscosity as the base polymer itself. When an aromatic-type oil were present, however, a markedly greater change resulted by heating the masterbatch in air. This effect was thought to result from a solubilization of the heavy metal by reaction with aromatic compounds in the oil which led to a catalytic oxidative scission of the polymer. Reynolds⁵⁷ reported that small additions of magnesium or calcium stearates, or naphthenates, would effectively neutralize this oxidative scission.

Another effect of the oil that may ascribed, in part, to the chemical nature of the extender is the influence shown on processability as related to the rate of breakdown of the rubber, rate of incorporation of pigments and the temperature coefficient of viscous flow. The aromaticity of the extender is directly related to the chemical compatibility of the extender and the polymer. It affects the oxygen absorption of the masterbatch as well as the rate of work and the temperature developed during mastication of the oil-extended rubber under

TABLE IX

COMPARATIVE AGING OF BASE POLYMER WITH 0.10 PART OF ADDED FERROUS SULFATE IN THE PRESENCE OF VARIOUS OILS AND STABILIZERS*

Softener (45 parts)	Antioxidant (1.25 parts)	No. of runs	Hours at 150° F			
			3.5	6.5	15	25
			% Retention of viscosity			
Sundex 53	BLE	2	89.6	87.5	72.1	69.2
Sundex 53	Stalite	1	86.8	77.5	73.1	—
Sundex 53	Polygard	1	84.6	78.7	68.1	57.5
Circosol 2XH	BLE	2	92.8	90.9	86.9	82.9
Circosol 2XH	Polygard	2	91.2	92.5	89.9	88.0
DOA	BLE	1	101.1	97.4	94.3	93.6
DOA	Polygard	1	101.1	97.4	94.3	93.6
Nil	BLE	1	97.0	98.0	95.6	91.6

* Reference 56, Table VII.

the applied rate of shear. These several effects have been investigated individually by Taft^{58, 59, 60} who examined the effect of chemical composition of extenders on the breakdown and aging characteristics and Gale⁶¹ who demonstrated effects on the power consumption during mastication. While the relative importance of these effects is becoming more apparent as a result of these investigations, it must be recognized that, because of the many interrelated factors involved, the most productive approach is still a subjective one involving simulated factory mixing operations and a relative rating for the ease of mixing and shaping of a particular extender-polymer combination.

Some generalizations can be made with respect to the extender contribution. It appears that a gradation in chemical characteristics is desirable in the extender as well as in the polymer and fortunately, this is inherent in the composition of a petroleum oil. A proper combination of chemical compounds that will include a high degree of solubilization, moderate sensitivity to oxidative chain chain scission, and high wetting power should be balanced by some incompatibility to provide a desirable degree of lubricity, chemical inertness to provide stability and a noninterference in carbon black-polymer reactions as well as in the vulcanization reaction.

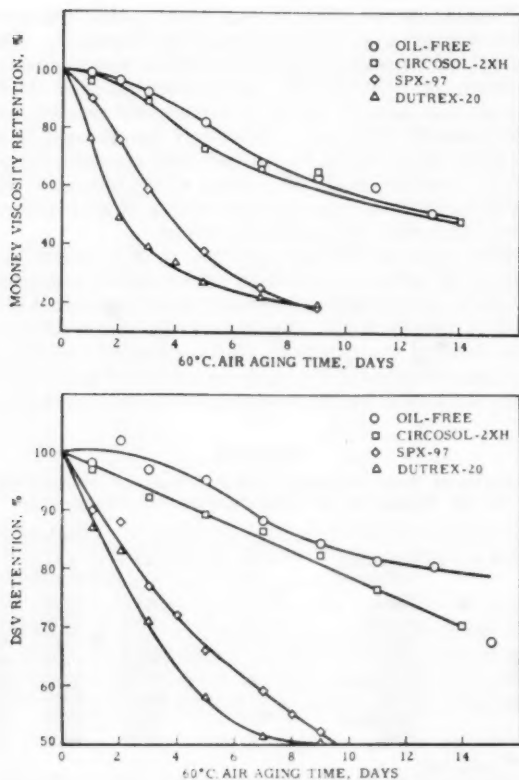


FIG. 7.—Retention of Mooney viscosity and dilute solution viscosity of oil-extended rubber during heat aging (37.5 parts of oil; iron pyrophosphate recipe). (Reference 57, Figs. 1 and 2.)

The chemical characteristics of the extender might be expected to have a direct influence upon the vulcanization reaction. The saturated or aromatic hydrocarbon compounds present in treated petroleum oils are relatively inert in this reaction. Indeed, it would be expected that they might provide some activation effect by solubilizing and improving the distribution of accelerators and sulfur throughout the compounded rubber and many workers have expressed the belief that there should be a compensation for the purely dilution effect of the oil loading on the concentration of curatives. As pointed out by Rostler⁹, nitrogen base compounds in the oil may exert an accelerating effect on the reaction. With the exception of the very aromatic types of extender oil, the content of nitrogen does not exceed 0.25%⁶². The actual balance of these effects would indicate that the usual oil extender is a neutral factor in the vulcanization reaction and no allowance need be made in this respect.

There are other extender materials, however, where a definite effect on vulcanization would be more likely. The asphaltene types mentioned by Rostler⁹ have a definite affinity for sulfur that may be expressed as a preferential

solubility or a mild chemical reactivity. The rosin acids, aliphatic-unsaturated vegetable oils, alkyl aryl esters, pine tars, coumarone-indene resins, etc., have well-recognized influences on vulcanization reactions that require some form of compensation in the compounding recipe.

A further chemical fact is the influence of the extender on the stiffening of the vulcanizate when exposed to low temperature⁶². The degree to which this phenomenon may be attributed to purely chemical factors is a limited one. It must be recognized however, that the chemical substituents in the extender molecules may affect this property to the degree that they influence the chemical compatibility of the extender-polymer combination. The presence of highly polar groups in the extender molecule may lead to significant effects at low temperatures, such as reported by Breitman⁵¹.

Certain chemical groupings in extender materials⁶³ are prone to form conjugated ring structures under the action of ultraviolet light, oxygen, heat, etc. These chemical compounds are colored and their formation results in a "discoloration" of the rubber product or a "staining" of a surface with which it may be in contact. Aromatic substances are a prime source of such effects particularly those that absorb light at a wavelength around 260 millimicrons⁶⁵.

(b) *Physical Characteristics*

The physical characteristics of the extender play the major role in determining the suitability of the material, the physical behavior of the masterbatch and the physical properties of the vulcanized product. In this section attention will be directed towards the physical characteristics of the extender that have been reported to affect their use and a more detailed discussion of the effects will be given in another section.

Kurtz and coworkers^{48, 49, 64} have provided a comprehensive survey of the physical properties of a range of commercial petroleum products (Table VI). The three basic chemical classes of substances present in petroleum oils are present in different ratios in the series of extenders that are designated as "relatively paraffinic", "relatively naphthenic" and "relatively aromatic". A continuous progression in physical characteristics may be encountered in this series. It should be understood, however, that this series of naturally-occurring substances occupy a band in a three-dimensional space describing the composition according to carbon type, i.e., paraffinic, naphthenic, and aromatic carbons (Figure 8). Synthetic combinations may be obtained to a limited degree by blending dissimilar oil compositions but this practice is not a particularly beneficial one either from the point of economics or of physical properties.

The basic characteristics of an extender that are significant in an extended rubber have been mentioned in a previous section as the shape and size of the molecule. The physical properties of the extender are determined by a number of test procedures⁶⁶ and these various estimates of size and shape as well as chemical factors, show a good relationship to the physical characteristics of the extended rubber⁶².

The molecular type analysis identifies the ratio of paraffinic, naphthenic, and aromatic hydrocarbons and may be used to estimate the weight ratio of ring and straight-chain structures in the oil (Table V). A closer estimate may be obtained from a carbon-type analysis that provides values for the ratio of ring and chain structures associated in the average aromatic and saturated molecules. These ratios may be used to demonstrate that the low temperature flexibility⁶² of the masterbatch is directly related to the percentage of chain

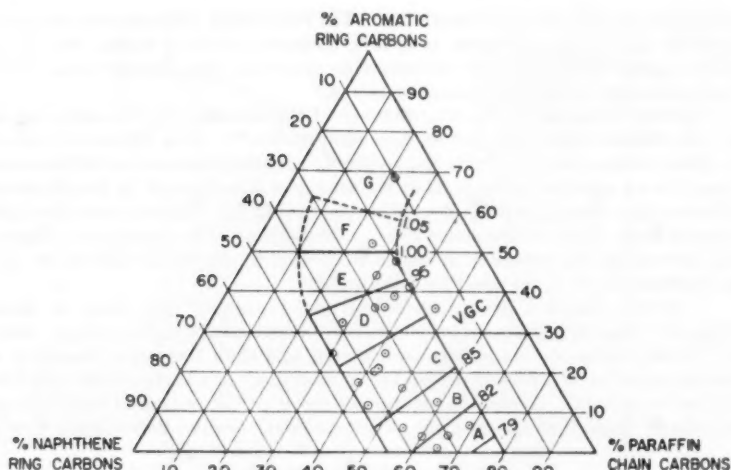


FIG. 8.—Carbon-type composition of petroleum oils. (Reference 49, Fig. 1.)

structures in the oil or inversely proportional to the number of rings. This indicates that flexibility is primarily associated with the separation of the polymer chains by the oil molecule and is affected by the average chain-to-chain distance as well as the mobility of the material occupying the interchain space. Reduced to measured oil properties, these ideas are expressed by the values for density and molecular weight or contained in the viscosity-gravity constant (V.G.C.)⁴⁴. The latter is a primary coefficient for estimating the suitability of an extender since it describes the primary factors given above. The V. G. C. value (Table X) ranges from 0.80 for relatively paraffinic oils to 1.00 for relatively aromatic oils with naphthenic oils having an intermediate values between

TABLE X
RELATION OF V.G.C. TO THE COMPOSITION OF PETROLEUM OILS*

V.G.C. class	Name	V.G.C. range	Approximate range for % carbon type ^a		
			% Cp	% Cn	% Ca
A	Paraffinic (Pennsylvania)	0.790-0.819	75-60	20-35	0-10
B	Relatively paraffinic (Mid-Continent)	0.820-0.849	65-50	25-40	0-15
C	Naphthenic (Gulf Coast)	0.850-0.899	55-35	30-45	10-30
D	Relatively aromatic	0.900-0.949	45-25	20-45	25-40
E	Aromatic	0.95-0.99	35-20	20-40	35-50
F	Very aromatic	1.00-1.05	(25)-0	(25)-0	50-60
G	Extremely aromatic	Above 1.05	Below 25-0	Below 25-0	Above 60

* Ranges do not necessarily apply for very narrow fractions or pure compounds.

* Reference 49, Table II.

TABLE XI
CORRELATIONS BETWEEN VULCANIZATE PROPERTIES, VOLUME LOADING OF OIL AND
VISCOSITY OF OIL FOR REPRESENTATIVE TYPES OF OIL
(TABLES V AND VI)*

[Physical property = $a + b$ (volume fraction of oil) + $c(\log_{10}$ viscosity of oil at 210° F) (cs)]

Property	a	b	c
Vulcanizate heat loss at 300° F, %	75.9	-159.4 ^a	-14.1 ^a
TR-10, ° C	29.0	-248.2 ^a	9.3 ^a
TR-70, ° C	45.9	-255.0 ^a	7.5 ^a
Tests at room temperature			
Tensile strength, lb/sq. in	9363	-20243 ^a	199.
Elongation at break, %	1104	-2119 ^a	70.4 ^a
Rebound, Bashore, %	-8.3	159 ^a	-6.5 ^a
Flex life, kc/in	22.1	-71.3 ^b	16.9 ^a
Heat build-up, ° F	100.0	-122.5 ^c	4.15 ^c
Tests at 205° F			
Tensile strength lb/sq. in	6080	-13679 ^a	6.7 ^b
Elongation at break, %	1001	-2106 ^a	29.0 ^b
Rebound, Bashore %	22.25	101.0 ^c	-3.3 ^c

^a Significant at 99% confidence level.

^b Not significant at the 95% confidence level.

^c Significant at the 95% confidence level.

* Reference 62, Table VI.

0.85 and 0.90. This constant combines factors relating to the density and the viscosity of the oil.

The density of oils range from 0.85 for relatively paraffinic types to just above 1.0 for relatively aromatic oils and, hence, this value provides an easy screening tool to identify the nature of the oil extender. The properties contributed by an extender are primarily related to the volume ratio of extender in the rubber masterbatch⁶². The density of the extender, therefore, is a prime variable in providing a knowledge of both the economical and technical factors associated with its use. Many investigators have analyzed the characteristics provided by the three classes of oil on a basis of their chemical composition when it would have been more productive to discuss these materials relative to the primary factor of volume loading (Table XI). Indeed, on an equal

TABLE XII
TREAD WEAR RATINGS FOR FACTORY-MIXED COMPOUNDS CONTAINING 50 VOLUMES OF
VARIOUS REPRESENTATIVE TYPES OF OIL*

	Sundex 53	A1	A2	S1	S2	S4
Rubber	100	100	100	100	100	100
Oil	50	50	49	44.5	45.5	43.5
Carbon black	75	75	75	75	75	75

(Tires, 6:70 X 15; 24 lb pressure; 16,800 miles)

	Sundex 53	A1	A2	S1	S2	S4
Rating, %	100	100	104	99	99	100
Durometer	66	71	67	72	67	68

* Zinc oxide, sulfur, and accelerator content did not vary.

* Reference 62, Tables VI and X.

volume loading (Table XII) there were no significant differences in the hardness or tread wear of masterbatches containing any of these oils.

The viscosity of an oil ranges from 20 centistokes at 100° F for relatively paraffinic oils to over 3000 centistokes for aromatic types. The viscosity may be interpreted in terms of the molecular weight of the oil and, hence one may draw conclusions on the volatility and mobility characteristics of the extender. The latter property is probably the one that has a secondary influence upon the volume of oil that may be used to achieve a selected level of masterbatch properties. It has been reported⁶⁴ that at a constant V.G.C. value, a higher molecular weight oil may be employed at somewhat higher loadings without any appreciable change in the properties of the masterbatch. The viscosity of the oil⁶² is inversely related to the heat loss of the masterbatch and vulcanized product and the resilience of the vulcanizate, but directly related to its flexibility at low temperatures and to the elasticity and resistance to crack growth of the vulcanized masterbatch.

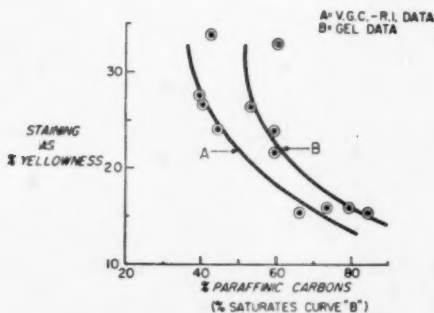


FIG. 9.—Staining characteristics of white oil-extended rubber vulcanizate relative to type of oil-extender. (Reference 42, Fig. 9.)

The light absorption characteristics and refractive index of the oil have a bearing upon the color of the extender-polymer combination⁶⁴ as well as the color and clarity of the vulcanizates containing various loadings of white and light-colored fillers or organic dyes. Oils which show a significant absorption of light at wavelengths around 260 millimicrons⁶⁵ tend to form conjugated ring structures under such exposure resulting in a discoloration of light-colored compounds with the development of a yellow discoloration. In addition, these compounds which are most prevalent in aromatic-type oils lead to a staining of other materials through contact and subsequent exposure to ultraviolet light. The relatively-paraffinic type oils show the least tendency to discoloration (Figure 9) and the effect is proportional to the percentage of paraffinic carbons in the oil.

(c) Blended Compositions

There are two classes of extenders in addition to petroleum oils that have been given considerable attention in this field. It seems pertinent to include the two classes, ester plasticizers and rosin acids, in this section. The art of compounding is well-versed in the practice of blending similar classes of material to modify specific properties and accepts the additivity of physical character-

istics, at least in a general way. It may be reiterated that petroleum oils are in reality a blend of three classes of hydrocarbon substances whose members constitute a multitude of various chemical groupings in endless permutations and combinations. The mere fact that a lesser volume of another class of substances were blended with an oil should not give rise to the expectation that any startling new physical concepts should be involved although somewhat different chemical attributes might be contributed by the additional substance. This statement may be considered as an underlying basis for the normal compounding practice of admixing minor amounts of different softeners, antioxidants, accelerators, or even fillers on the understanding that the physical effects are largely additive.

An oil-extended SBR masterbatch will contain about 5% of a fatty acid, a rosin acid or a blend of these two substances that are derived from the emulsifier used during polymerization. These materials are extenders for the SBR polymer hydrocarbon and they serve useful purposes in the product, e.g., as plasticizer, tackifier, dispersant agent, vulcanization aid, scorch retarder, etc. It is advantageous, indeed, that such substances should be "masterbatched" in the SBR in the process of its manufacture since an extreme state of distribution and dispersion is a basic requirement for their optimum performance in one or more of these varied functions. These minor quantities of extender are soluble in oil and appear as part of the extender loading when the masterbatch is extracted by ethanol-toluene azeotrope. It is the practice, of course, to subtract the emulsifier acids from the extract in order to calculate the actual oil loading and base it on 100 parts by weight of standard SBR product⁶⁷. This is just an artifact and forms a part of the accepted practice of the compounding art. There is no doubt that the emulsifier acids are extenders and act as such. It is general practice to add sundry other softeners in minor amounts to oil-extended rubber compounds. These also form a part of the total volume of extender albeit they may contribute other specific characteristics to the final compound, i.e., altered tack, mold flow, roll sticking, activated cure, etc.

In one case a rosin acid⁶⁸ was used as the principal extender for high molecular weight SBR and, indeed, it provided vulcanizates with a high tensile strength and good wear resistance, as would be predicted by the theoretical concepts described above. An investigation of rosin acid as an extender in SBR masterbatches⁶⁹ was made to confirm the trends that were anticipated for blends of oil and rosin when employed as a combination extender. It was noted that the principles described above were pertinent in the case of rosin acid alone or to its blends with petroleum oil. One fact seems worthy of comment, however. When the oil to rosin ratio in the final compounding recipe exceeded about 1:7 the total extender had a behavior similar to that of an equal volume of oil. The physical state of the extender blend at room temperature was, apparently that of a liquid.

Various alkyl-aryl esters^{70, 71} have been employed as extenders in high molecular weight SBR polymers in order to improve the flexibility of the vulcanizate at low temperature. Most of these substances are liquids and the physical effects of the size and shape of the molecule are similar to those described for a petroleum oil. It is not surprising, therefore, that blends of ester-type and petroleum softeners behave in a similar manner over the entire blending range⁶⁹.

Another phenomenon associated with the properties of the extender, but dependent to some extent on the characteristics of the SBR polymer, is the

rate and degree of plasticization of the high molecular weight polymer fraction that occurs through addition of a fixed volume of extender oil. In the section on polymer characteristics, this factor has been related to the *oil demand*⁷². As pertains to the extender, this factor is named *oil efficiency*⁷². It should be understood that the oil demand is measured by the amount of ETA-extractable material in an extended rubber having a masterbatch Mooney viscosity of 53.5. The distinction between the total extractable, nonpolymeric material and the actual amount of added oil is not clear in some of the early reference to oil loading and oil demand. As pointed out in this review, the ETA-extract of an extended rubber is composed of a small amount of material from the contained rubber (5 to 6%) the emulsifier for the extender (1 to 2% based on the extender) and the extender. The oil demand value may be employed to estimate the amount of a reference oil that is required to give a masterbatch Mooney viscosity of 53.5 for a certain SBR polymer [See Section IV A (b)]. The "oil efficiency" defines the amount of another oil as a percentage of the amount of the reference oil, that will give a masterbatch viscosity of 53.5 for the same SBR polymer. The "oil efficiency" value, similarly, is based on the weight ratio of the ETA-extract values in the two cases. The choice of a reference oil is not critical but, since the first commercial oil-extended rubber employed an aromatic-type oil (Sundex 53), this oil has been adopted as a reference oil with a designated oil efficiency of 100%.

Rooney⁷² has measured the oil efficiency values for a number of commercial oils and related these values to the viscosity-gravity constant. The weight efficiency of oils appears to be directly related to the V.G.C. of the oil (Figure 10), and, hence a maximum for the highly aromatic type. The density of the oil varies directly with the aromaticity of the oil so that a maximum on a volume loading basis will appear in the region occupied by the naphthenic-type oils.

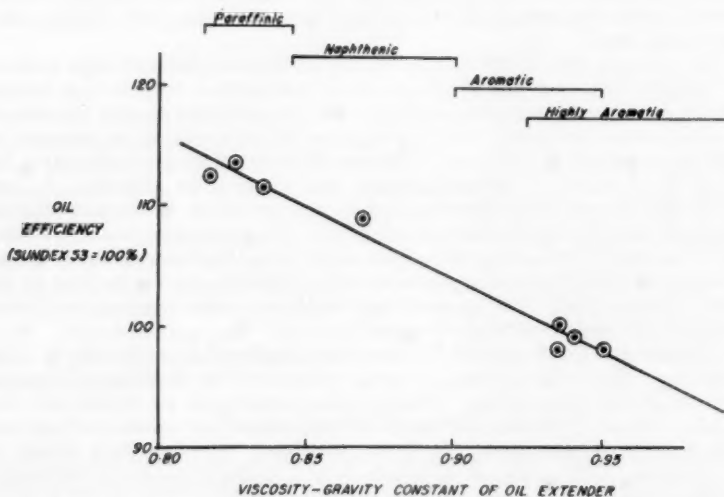


Fig. 10.—Relationship of viscosity gravity constant and oil efficiency (Reference 72, unpublished).

The oil efficiency value provides a basis for comparing products formed by blends of oil material from different sources, or from different refining processes. It may be employed to compare different classes of extenders (rosin acid, oil, ester, etc.) as well as blends of different classes on a common basis.

C. PIGMENT CONTRIBUTION

The contribution of the pigment in an oil-polymer system^{73, 74, 75} has an important influence upon the quality of the vulcanized product. This statement is obvious, of course, when applied to any rubber that is to be compounded to produce the maximum performance under extreme service conditions. In the case of an oil-extended rubber, however, there is a definite requirement for the use of pigments with a relatively high surface area and a relatively high structure. These properties are those expressed by the term "oil absorption" as commonly used by the carbon black industry⁷⁶. As discussed later oil-extended SBR¹¹ was designed to provide a first-grade HAF tire tread compound when the carbon black was employed at the same loading based on the total of oil plus rubber as would customarily be used based on the rubber with a standard type of SBR. In the case of coarser fillers with a low degree of structure the compounding recipe must be designed to suit the masterbatch on the basis that the compounder is dealing with a new type of rubber having a different set of physical properties. This does not involve any radical or elaborate approach but merely indicates that it is not likely that a simple arithmetical ratio can be selected to adjust filler loadings in designing an oil-extended rubber recipe to replace an SBR recipe when the rubber hydrocarbon content is less than, say, 50%.

As reported by Yanko³⁶ about 30% of standard GR-S is composed of polymer having a molecular weight below 30,000. This material can be cross-linked by sulphur and is loosely bound into the network of higher molecular weight rubber. Its contribution to the network³⁸ is limited, however, because it introduces two free ends into the system but only adds a short chain length. The net contribution is not different from that of a diluent. Replacement of this low molecular weight polymer by an oil softener has an equivalent effect except that there is no possibility of chemical crosslinking the oil into the network. In order to compensate for this difference some physical forces must be engendered or else the net effect on reinforcement might be negative. The compatibility between the oil and polymer provide attractive forces of some magnitude but a similar attraction must exist between the oil and filler in order to compensate for the degree of bonding provided by the low molecular weight polymer. A fine particle size carbon black with an average oil absorption provides the required level of physical forces to associate carbon black, oil and polymer into a continuous physical and chemical network. This point may be demonstrated by comparing the behavior of EPC and HAF carbon blacks at a 50 part loading in oil-extended rubber¹¹. There are only minor differences in the physical properties of the HAF compound compared to those of a 50 part HAF SBR compound. The EPC oil-extended compound, however, is slower curing and has a considerably lower modulus and tensile strength than a similar SBR compound.

The carbon black is "wetted" much more rapidly by the oil than the polymer hydrocarbon and the ultimate distribution and dispersion of carbon black is improved in an oil-extended rubber. Harrington¹¹ and Buckler⁴² report that 30 parts of HAF carbon black provide the optimum tensile strength for oil-

extended rubber compounds whereas about 40 parts are required in a cold SBR type⁷⁵. Advantage is taken of this ability to wet and disperse carbon black to prepare oil-extended rubber compounds with even the higher reinforcing types of carbon black (SAF).

The formation of bound rubber is not interfered with by the presence of the oil. An oil-extended rubber does not develop as much heat during the mixing operation, however, and this effect could lead to a lower bound rubber content when the same mixing cycle is employed as that for cold SBR. Observations on the crumbly nature⁷⁷ of an oil-extended rubber-carbon black mix during an early stage in mixing suggests that the carbon black tends to absorb the oil faster than the loose black can be dispersed in the polymer phase, and that the dispersion of the oil-loaded black occurs at a second stage during mixing. Quite dry, boardy compositions⁶¹ have been observed in factory mixes that have been prepared by rapid, high-pressure mixing procedures for the minimum time required for incorporation of loose carbon black. Subsequent milling operations have rapidly converted this composition into the normal plastic, glossy black mix. This type of behavior has been noted by Harrington¹¹ who observed that the compound Mooney viscosity of Banbury-mixed oil-extended rubber tread stocks is initially higher than that of cold SBR tread mixes and that the Mooney viscosity progressively decreases during each processing operation through to the final extrusion of the tread section. This behavior suggests a gradual redistribution of the oil as the carbon black-polymer forces are built up and the carbon black is progressively dispersed on a finer scale throughout the mix.

Such a process indicates that an added advantage exists for forming a masterbatch of the three components at the latex stage. Indeed, a small additional amount of oil is added in preparing a carbon black masterbatch with an oil-extended rubber in recognition of the dispersing power of the oil. In this case, the process oil has replaced the previous use of naphthalene or ligno sulfonic acids salts which are reported to produce some adverse effect upon the vulcanization reaction.

D. MASTERBATCH DESIGN

The first commercial oil-extended rubber¹¹ was produced by blending a high Mooney viscosity cold SBR polymer with an aromatic-type oil (Sundex 53). This masterbatch contained about 45 parts of oil per 100 parts of polymer and it was developed to produce a compound Mooney viscosity of 60 when 100 parts of the masterbatch was compounded in a Banbury mixer with 50 parts of HAF carbon black in a simple tread-type recipe. This simplified design was selected to allow an easy substitution of the oil-extended rubber in tread compounds, either on a partial or complete replacement basis, and in the type of compound being employed for cold SBR in 1950.

Preliminary theories³⁸ on the function of the low molecular weight fraction in SBR with respect to processing characteristics and reinforcement provided a basis for subsequent refinements without any significant departure from the basic design.

It is of interest in an historical sense to note that other workers in this field adopted as a design basis the requirement that the raw polymer plasticity of the masterbatch, either Williams plasticity or Mooney viscosity, should be comparable to that of standard SBR. Thus, the early work of Rostler⁹ proceeded from this point of view. D'Ianni¹² in the work carried out at Goodyear Tire and Rubber Company also selected this design basis and attacked the

development on a more gradual, but wider, scale. This work resulted in the first American oil-extended rubber produced under the authority of the Office of Rubber Reserve⁷⁸. Two products first appeared; X-628 a 25 part oil masterbatch and X-629 a 25 part oil—50 part HAF carbon black masterbatch. After factory trials in the United States had confirmed the ability of the X-628 masterbatch to provide tread compositions of satisfactory performance, a second step was taken to prepare an oil-extended product containing 37.5 parts of aromatic oil per 100 parts of polymer⁷⁹. This product was designated as GR-S 1710 in July, 1953.

Concurrent investigations in Canadian rubber factories showed difficulties in handling the tread mix upon discharge from the Banbury mixer and in the opening of tread splices in tire building operations. Similar difficulties were reported in the United States⁷⁷. These factory problems gradually were mastered by modifications to factory equipment and operations and by im-

TABLE XIII
PHYSICAL PROPERTIES OF SOFTENED AND STANDARD OIL-EXTENDED RUBBER*

	Parts	
Masterbatch	100.0	
Philblack O	50.0	
NBS stearic acid	1.38	
NBS zinc oxide	3.45	
Santocure	0.86	
NBS Sulfur	1.38	
Sample	Krynol	T-8158
ML/4'		
Unsoftened	56.5	54.0
When tested	56.5	38.5
Compound	63.0	41.5
Tensile (50-min cure) at 292° F	3350	3100
% elongation (50-min cure)	550	480
300% modulus (50-min cure)	1650	1900
Shore hardness	49	51
Extrusion		
Rate, g/sec	13.28	18.13
Ratio, g/inch	0.413	0.389
Added FeSO ₄ ·7H ₂ O, part	Nil	0.025

* Reference 56, Tables X and XI.

provements in the control of production methods in the synthetic rubber factories. By 1955, however, the adoption of high-speed, high-pressure Banbury mixing procedures, required to increase the mixing capacity of the factory equipment, created a more difficult problem for the oil-extended polymer⁸¹. In such short mixing cycles the oil-extended rubber did not reach as advanced a stage of incorporation and dispersion of carbon black as was attained by a cold SBR. The actual difference in the state of incorporation was not large but the effect upon automated production lines could be quite serious since shut-downs through stock failure could result in a significant decrease in the volume of production.

These difficulties led to the development of laboratory tests to simulate factory mixing operations in order to increase the rate of preliminary incorporation of carbon black in oil-extended rubbers^{81, 80}. Buckler⁴² summarizes the investigation that showed the adverse effect of very high molecular weight

polymer on the rate of mixing and lead to the development of an improved processing masterbatch. The oil loading in the Canadian product was adjusted to 37.5 parts at that time in the interests of standardization. The original masterbatch containing 45 parts of oil pioneered the way for the present, higher oil content masterbatches that encounter less severe manufacturing practices in applications for mechanical goods⁵¹.

It is of interest that during the detailed investigation of processability at Polymer Corporation Limited it was discovered that a significant advance was possible by extending a slightly lower average molecular weight polymer with 37.5 parts of oil to achieve a lower Mooney viscosity level of about 45. Not only was the rate of acceptance of carbon black much-accelerated but there was no significant change in the wear resistance of the vulcanizate evidenced in numerous tire tests. This development originated in the significant observation reported by Mitchell⁵⁶ that the original oil-extended rubber and those "heat softened" as a result of the inclusion of trace amounts of heavy metals did not show any appreciable difference in physical properties after vulcanization (Table XIII). Similar effects have been noted after thermal degradation of Buna S-3²⁴ and SBR³⁰. The physical effects suggest a preferential scission of the longer chains with an efficient repair mechanism to combine the large fragments into the network during vulcanization.

In retrospect, one may find it interesting to compare the progress of development in the U. S. and Canadian synthetic rubber plants. The American program commenced with a low (25-Part) oil loading and "heat softening" was a prevalent difficulty according to literature reports⁵³. This effect may have been beneficial to the adoption of oil-extended rubber in the more-mechanized tire factories of the United States. In any case, the presence of such instability resulted in a greater breakdown of the rubber under high-shear and reduced many of the problems in mixing and shaping operations. It did, however, slow down the tendency to employ high oil loadings in masterbatches designed for tire applications and imposed a ceiling loading at about 37.5 parts. In Canada, the primary emphasis was placed upon the production of an oil masterbatch having an equivalent stability to that of cold rubber. This design basis was maintained throughout the development to improved processability and led to an understanding of various factors in the polymer composition that enabled a rapid introduction of "super processing" low Mooney viscosity masterbatches at the standard oil loading of 37.5 parts.

The problem of designing high Mooney viscosity polymers capable of accepting oil loadings above 37.5 parts without sacrifice of processing or performance qualities is no doubt a matter being given some attention by the synthetic rubber producer at the present time. In order to take further advantage of the lower Mooney viscosity approach, some radical changes will be necessary in production methods because the plasticity of the coagulated crumb is quite high at the drier temperatures and this could impose a restriction on the production rate with present equipment. The design of stable, high Mooney viscosity rubbers that will accept up to 100 parts of oil is no real problem providing that the properties of such a product do not restrict the production rate in factory mixing equipment. Progress in this direction is limited at the present time by the mixing efficiency of factory equipment. The rubber industry has seen the amazing progress of the Banbury mixer towards higher volume capacity during the past fifty years. Progress towards equipment of higher mixing efficiency is the current need and it will set the stage for further advances in the design of oil-extended rubbers.

(a) *Mode of Blending*

An important precaution in the compounding of polymer with large quantities of both fillers and softeners has been that the latter should not be added to the mix simultaneously³². The general practice recommended by many compounders has been to alternate additions of filler and softener when large quantities of both are required and this procedure apparently provides optimum speed of mixing without subjecting the polymer chains to excessive work that would lead to a high degree of breakdown of the rubber portion.

Rostler⁹ reports early studies of the mixing of large proportions of extender on the filler dispersion and he concluded that the degree of filler dispersion was not adversely affected regardless of what amounts of softener and filler were co-coagulated or premixed with the polymer.

A compounding study made in the Philblack Sales Service Laboratories in Akron, Ohio⁹, shows that the masterbatching of low temperature SBR with softener did not impair the filler dispersion. The stress-strain data for tread-type compounds prepared with a softener-polymer masterbatch were very similar to those secured by a conventional mixing procedure.

Early investigations carried out in England²⁹ showed that standard hot GR-S could be softened by allowing the sheeted polymer to soak in oil overnight and that at least equivalent physical properties were obtained when compared to mechanically-broken down GR-S mixed to the same compounded composition.

Later, extensive investigations^{11, 41, 62, 66, 82} were made to determine whether better physical properties would result from the addition of softener to a high molecular weight SBR rubber by (a) addition at the latex stage and co-coagulation, (b) preparation of a masterbatch of the softener by mechanical mixing of the dry polymer or (c) soaking the dry polymer crumb or sliced polymer in oil. None of these evaluations (Table XIV) (Table XV) indicated that any particular differences in the vulcanizate properties would be produced by any

TABLE XIV
STRESS-STRAIN DATA OF COMPOUNDS PREPARED BY DIFFERENT MIXING METHODS*

Cure time (min at 287° F)	15	30	45	60	90
			Compound A (Dry mixed)		
Modulus, 300%	420	1050	1195	1300	1420
Tensile (psi)	1080	2575	2940	2890	2910
Elongation, %	860	670	600	570	540
Durometer hardness	49	55	58	58	59
			Compound B (Rubber-oil latex mixed)		
Modulus, 300%	310	1110	1240	1360	1475
Tensile (psi)	900	2820	3100	3210	3180
Elongation, %	920	680	610	560	520
Durometer hardness	46	55	59	59	60
			Compound C (Rubber-oil-black latex mixed)		
Modulus, 300%	No Cure	690	1040	1110	1285
Tensile (psi)		2500	3100	3115	3270
Elongation, %		690	620	590	570
Durometer hardness		53	57	57	58

* Reference 41.

TABLE XV
COMPARISON OF FACTORY PROCESSING AND PHYSICAL TEST DATA FOR TREAD COMPOUNDS PREPARED FROM BANBURY-MIXED OR LATEX-MASTERBATCHED RUBBERS**

Test No.	3101			3135			3179		
	XPRD-211 135	XPRD-211 135	XPRD-211 135	X 598* 39	Krynd 135	Dry mix	X 598* 39	X 698† 130	Krynd 135
Polymers tested									
Computed Mooney									
Method of mixing									
Variables									
Polymer	100	100	100	100	100	100	100	100	100
HAF black	75	75	75	50	75	75	50	75	75
Oil	50	50	50	8	50	50	8	50	50
Accelerators	1.3	1.3	1.3	std.	std.	std.	std.	1.1	1.15
Sulfur	2.1	2.1	2.1	std.	std.	std.	std.	2.0	2.0
Mixing cycle, No. 11 BB									
Masterbatch	10 min	5 min	6 min	5 min	7 min	7 min	5 min	7 min	7 min
Second master	3 min	3 min	3 min	3 min	3 min	3 min	3 min	3 min	3 min
Final batch RM	3 min	3 min	3 min						
Mooney viscosity MLA									
Masterbatch	145-139	145-130	111-103	84-75	136-122	98-87	84-75	137-126	131-118
Second master									
Finish	110-104	97-86	91-83	78-67	96-85	84-74	78-67	84-74	102-90
Final batch RM	85-80	76-70	85-77						81-72
Extruding tempera- ture, °F	275	270	275	285	280	270	285	270	270
Physical Properties									
Modulus @ 300% E									
30 min. @ 287° F	950	1225	975	875	1225		1000	725	1100
60	1600	1650	1500	1325	1750		1450	1375	1425
90	1500	1750	1625	1350	1900		1500	1400	1525
Tensile strength, psi									
30 min @ 287° F	2625	2825	3050	2650	3100		2675	2300	2825
60	3150	3150	2175	3725	2825		2400	2700	2300
90	2850	3200	2200	2775	2850		2675	2675	2125
Elongation, %									
30 min @ 287° F	595	525	600	720	580		640	640	600
60	510	480	410	540	450		450	430	470
90	475	470	420	570	410		500	480	500
Durometer hardness									
30 min @ 287° F	59	57	52	65	55		63	53	55
60	62	56	62	67	58		66	59	59
90	64	61	61	69	60		70	59	59
Rebound									
R. T.	52	56	58	56.9	54.9		58	55.4	56.9
212° F	68.1	72.3	75.2	63.1	68.4		63.1	68.4	70.7
Treadwear rating	100%	106%	106.5%	100%	116%		100%	107%	127%

** Reference 11, Table XIV.

* SBR cold-rubber-oil-black masterbatch.

† SBR cold-rubber-oil-black masterbatch.

of these methods of adding the softener to the polymer. The addition of large quantities of oil to dry polymer and carbon black in a Banbury mixer (Table XV) required a longer time of mixing than when a latex masterbatch was employed and, generally, resulted in higher compound Mooney values.

The method best-suited to commercial operations is one that allows the continuous, large-volume production of a uniform quality material having a controlled ratio of softener to polymer. This may be achieved by large-scale dry-mixing of the oil and polymer but the process would be a batch-system and some variation in oil loading might be expected between batches.

The oil-extended rubber is produced commercially⁷⁸ by a fluid blending of the synthetic rubber latex with an oil emulsion, the so-called latex masterbatch operation. This process provides means to ensure that an accurate ratio of oil to polymer is intimately mixed and subsequently, co-coagulated to form a homogeneous masterbatch. The latex masterbatch process not only provides a uniform product but enables the producer to prepare any desired combination of softener and synthetic rubber by using the same equipment and procedure.

(b) Tread-Type Masterbatch

The design of an oil masterbatch for use in tire treads was the objective of the first oil-extended rubber. Buckler and Mitchell⁴² have provided a detailed

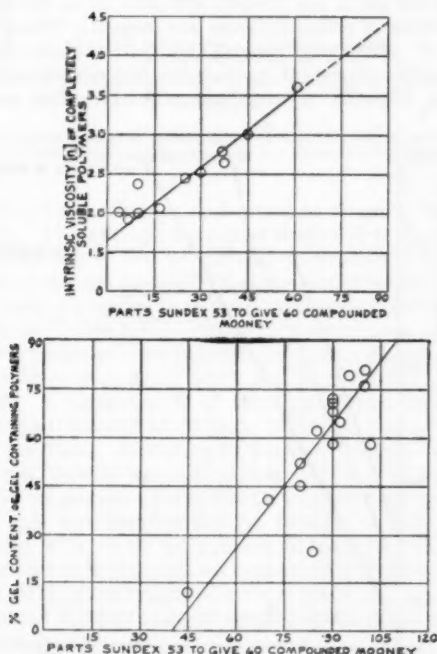


Fig. 11.—Oil loading required to produce a 60 compound Mooney viscosity for soluble butadiene-styrene polymers and those containing gel (oil loading per hundred parts of polymer; 50 parts of HAF carbon black per hundred parts of polymer plus oil). (Reference 41, Figs. 1 and 2.)

account of the various steps in its development and these will be followed here to illustrate the principles involved. The preliminary decisions involved the selection of an available large-volume type of oil and the probable compounding recipe. An aromatic oil was selected because this class of oil was known to be quite compatible with SBR and, since staining stabilizers were used in SBR for tire applications, there was no necessity to seek a light-colored oil. The tread recipes in use at that time employed 50 parts of HAF carbon black per hundred parts of polymer and a suitable level of processability in the factory was achieved by a compound having a Mooney viscosity in the region of 60. It was logical that, if the oil replaced the low molecular weight fraction of the rubber, then instead of employing 50 parts of carbon black based on the rubber alone it should now be based on the rubber-plus-oil. Thus, the initial definition of oil demand¹¹ (Figure 11) was the oil loading required for a particular polymer to give a 60 compound Mooney viscosity when the carbon black loading is one-half the weight of polymer plus oil. When this basis was used to determine carbon black loading, it was found that the Mooney viscosity of the latex masterbatch of the aromatic-type oil and polymer (XPRD 211) was 53.5. This value was later adopted to define the oil demand of a high molecular weight SBR as being the weight loading of ETA-extractable material per hundred parts of polymer required to produce a masterbatch Mooney viscosity of 53.5.

The oil demand was found to vary directly as the intrinsic viscosity of the soluble polymer when gel is not present and directly as the gel content when appreciable quantities of gelled polymer are present. These correlations are shown in Figure 11. Other work reported by Taft⁶⁰ showed that the oil loading (Figure 12) required for a constant masterbatch Mooney viscosity varied directly with the Mooney viscosity of the base polymer. The intrinsic viscosity

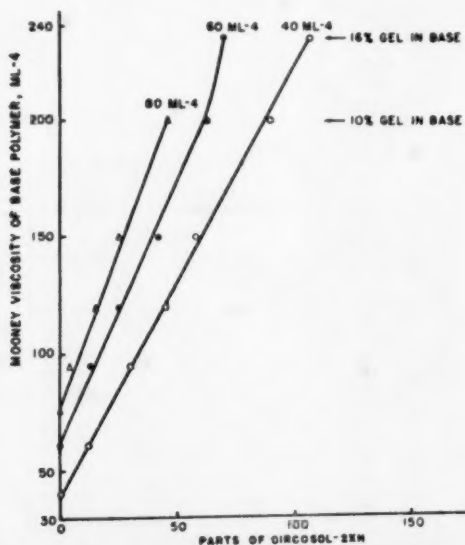


Fig. 12.—Balance of base polymer Mooney viscosity and oil loading to produce a constant masterbatch Mooney viscosity. (Reference 60, Fig. 1.)

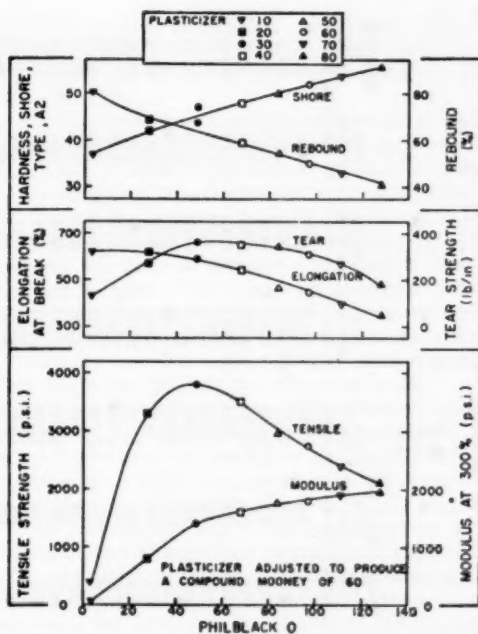


FIG. 13.—Variation of physical properties of vulcanizates of high molecular weight GR-S with HAF carbon black and softener adjusted to give a compound Mooney viscosity of 60. (Reference 11, Fig. 3.)

(toluene) of polymer requiring an oil loading of 25 parts is 2.45 and that of 37.5 parts is 2.85. The average molecular weight of the polymer may be increased still further but it will be difficult to produce a completely soluble polymer at higher levels and even very high molecular weight, ungelled polymer was found to present a problem in factory processing operations.

Vulcanizate data (Table XVI) (Figure 13) showed that the optimum tensile strength value was obtained for a polymer having an oil demand of 45 parts at a combination of 50 parts of HAF black and 30 parts of aromatic oil per 100 parts of polymer. A consideration of other properties, including treadwear, indicated an optimum balance at 75 parts of carbon black and 50 parts of oil per 100 parts of polymer. According to Buckler⁴² both of these combinations had a 60 compound Mooney viscosity and are in the acceptable processability range while the latter provides the optimum balance of physical properties.

The design basis was summarized by Buckler as follows:—"If a given polymer is blended with oil to the amount defined by its oil demand it will automatically possess an acceptable oil masterbatch Mooney. If the blend is then mixed with 50% of its weight of carbon black (HAF), it will possess an acceptable compound Mooney and will develop optimum balance of vulcanizate properties."

The high molecular weight SBR will show slight variations in the average molecular weight and molecular weight distribution when produced in different synthetic rubber plants and similar small variations in the aromatic oil may be

TABLE XVI
EFFECT OF VARIATION OF CARBON BLACK AND SOFTENER LOADING ON THE PROPERTIES OF OIL-EXTENDED RUBBER*

Phulblack O (phr)	Wycor (phr)	Circosol 2XH (phr)	Compound Mooney ML ₁ (212° F)	Mooney cure point (min @ 292° F)	Extrusion rate (cc/15 sec)	Die swell (%)	Press cure (min @ 292° F)	Hardness shore, Type A2 (30 sec)	Mod. at 300% (psi)	Ten. strength (psi)	Elong. at break, (%)	Tear strength (lbs/in.)	Rebound % (70 min @ 292° F)
40	—	—	55.5	14.9	12.3	177	70	44	1290	3460	570	360	60.4
50	—	—	65.0	15.0	16.5	160	60	48	1750	3350	500	360	55.3
60	—	—	75.5	13.2	15.8	148	55	53	2330	3200	400	340	51.9
70	—	—	91.5	11.3	14.5	134	40	63	2780	3060	330	310	46.3
40	—	5	47.0	16.8	17.5	155	70	39	950	2840	600	315	63.0
50	—	5	54.5	15.7	16.8	156	65	45	1450	2820	500	345	57.7
60	—	5	64.5	14.8	16.9	144	60	51	1940	2760	380	330	51.0
70	—	5	66.0	13.3	17.0	126	55	57	2460	2750	325	320	47.7
40	—	10	41.5	16.8	16.8	156	55	37	800	2380	605	290	61.5
50	—	10	47.0	16.9	16.5	150	65	41	1130	2380	505	310	56.3
60	—	10	56.5	15.3	16.5	145	75	51	1700	2060	470	345	49.0
70	—	10	67.5	14.6	16.4	133	65	54	2080	2650	395	305	46.3
20	20	5	49.0	19.8	16.2	163	50	40	680	3420	800	305	57.8
25	25	5	55.5	18.3	15.4	166	65	44	1170	3320	660	345	52.3
30	30	5	65.5	16.7	15.1	153	60	49	1560	3200	550	345	48.1
35	35	5	78.5	15.0	14.6	139	70	53	1950	3030	450	310	42.8
—	40	5	48.0	22.3	14.3	162	70	37	525	3225	800	275	56.3
—	50	5	54.0	21.4	15.0	166	75	43	740	3450	770	320	50.6
—	60	5	64.0	19.8	14.5	164	70	49	980	3270	700	335	45.5
—	70	5	72.0	18.3	15.2	146	70	54	1225	2800	570	335	41.9

* Reference 11, Table VII.

expected when different crude oil supplies, or refining methods, are involved. An automatic compensation is made for such minor variations by the design practice of adding sufficient oil to the polymer to achieve a 53.5 Mooney viscosity for the masterbatch.

A recent trend⁸² in tire compounding has favored a "soft, quite tread" composition. It has been reported that this effect may be obtained by using a more aromatic type of oil and adding a lower quantity of either ISAF or SAF carbon black. In designing an oil-extended rubber to meet this new set of requirements it may not be necessary to make any change in the base polymer providing the two oils have about the same oil-efficiency, i.e., the same weight loading of either oil will give an average masterbatch Mooney viscosity of 53.5. An advantage is taken of the higher oil tolerance (or structure) of the ISAF or SAF carbon black to reduce the black loading from 50% to 45%, say, based on the total of polymer plus oil. This procedure will reduce the compound Mooney viscosity level but not the quality of the vulcanizate because of the higher reinforcing power of this type of carbon black.

A second method has been adopted, recently, to achieve an easier-processing oil-extended rubber as well as a desirable low-modulus vulcanizate. This design involves adding the normal loading of oil to a polymer having a slightly lower average molecular weight, i.e., adding a slight excess of oil over that predicted by the oil demand. This procedure results in a slightly lower Mooney viscosity for the oil masterbatch and a loading of between 40 and 45 parts of ISAF or SAF carbon black is employed to provide a slightly lower compound Mooney viscosity and maintain the easy processing characteristics in the compound. If this case is considered according to the theoretical design basis it will be seen that since the total quantity of diluent (oil plus carbon black) has been reduced, there should be no change in the quality of the vulcanizate. A more reinforcing type of carbon black has been employed, however, and this should show some beneficial effect on the overall quality of the vulcanizate.

The design of carbon black-oil-polymer masterbatches^{74, 84, 85, 86, 87} follows the same principles outlined above with one notable difference. In this case, the carbon black is given a preliminary treatment under high-shear conditions to break up the pellets and provide a suspension of finely-dispersed carbon black. This carbon black suspension is codispersed with the emulsified oil in the polymer latex and co-coagulated to give a predispersed carbon black masterbatch. The amount of breakdown of the high molecular weight polymer encountered during compounding operations is even less than that encountered during the mixing of the oil-extended polymer with dry carbon black. It is reported, that the carbon black structure also undergoes less change, not only because the mixing cycle is of shorter duration, but because the carbon black is already distributed in the oil-polymer matrix. These two factors would lead to a higher compound Mooney viscosity for the carbon black masterbatch product and somewhat more difficulty in extrusion and shaping operations. In essence, the high molecular weight polymer was not subject to the same breakdown and, hence, has an apparent higher oil demand in the compounded state and, to a degree, has been compounded with the same loading of a slightly more-reinforcing carbon black. In order to adjust for these differences in the design conditions, it has been customary to add slightly more oil to the same base polymer in producing a carbon black masterbatch while maintaining a loading of 50% of carbon black based on the masterbatch.

In the case of a carbon black masterbatch employing a more-reinforcing type of carbon black, i.e., ISAF or SAF, there are two possible approaches to the

design. One basis would be to maintain the same level of total diluent (carbon black plus oil) as employed in the case of HAF black. This procedure would result in a higher quality compound at a slight sacrifice in processability. It would be more desirable to achieve the same level of processability and physical properties by (1) making a small increase in the oil loading to compensate for the higher reinforcing power of the carbon black, or (2) by reducing the carbon black loading to less than 50% based on polymer-plus-oil. A third approach involves a combination of the two methods but this would probably introduce complications into the compounding design that are not warranted by the small saving in material or cost.

(c) *Processing Characteristics*

The literature on oil-extended rubbers contains numerous references to the "processability" of the polymer. This much-abused term has been employed to indicate any or all operational difficulties encountered from the initial breakdown of the raw polymer to the inspection of the vulcanized article. In the case of oil-extended rubber, there were several "processing" difficulties that were peculiar to the use of a high-molecular weight polymer extended with oil:

1. The oil masterbatch tended to "heat-soften" by a breakdown of the polymer in the presence of heavy metal ions⁵⁶.
2. The oil-extended polymer required a longer mixing time to incorporate carbon black and reach an equilibrium compound Mooney viscosity¹¹.
3. The compounded masterbatch was difficult to splice in tire building and required longer periods under stress, or higher forming temperatures, to give adequate splice adhesion⁷⁷.

The source of these processability problems is undoubtedly the fact that a high average molecular weight polymer was employed in the masterbatch. The basis for the masterbatch design was essentially one of economy of raw materials and equivalence of vulcanizate quality. It was recognized that processability imposed an upper limit on the molecular weight that could be considered for the polymer⁴². The rubber manufacturer, however, required a product that would process similarly to cold SBR. The occurrence of heat-softening imposed a control problem for the rubber producer, whether it occurred in the production operation or during storage of the product. It did alleviate some of the processing difficulties, however, and did not have a very significant effect on the quality of the vulcanizate (Table XIII). The rubber producers that had the least difficulty with heat-softening, however, had the most difficulty in achieving a satisfactory level of processability in the product.

That the basic difficulties were associated with an insufficient degree of mastication of the compounded masterbatch was confirmed a few years after the introduction of oil-extended rubbers. When shorter mixing cycles in high-speed Banbury mixers became a desirable practice, these same processing problems re-occurred and to a degree that could scarcely be overcome by the use of higher breakdown temperatures or the addition of small quantities of peptizers³⁰.

Indeed, a laboratory evaluation reported by Priklonskaya³⁸ that describes the effect of rotor speed, pressure, time and temperature variables, suggests that the major factor affecting the mixing characteristics of the oil-extended rubber was the elevated temperatures encountered in the short, high-pressure Banbury cycle.

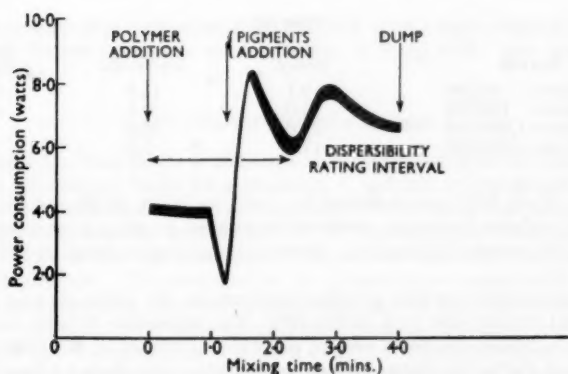


FIG. 14.—Hypothetical Banbury power curve. (Reference 61, Fig. 4.)

An investigation of the source of these difficulties was reported by Gale⁶¹ who outlined the first laboratory test method for evaluating the processing quality in a laboratory, Type B, Banbury mixer. This procedure simulated the factory mixing procedure on a small scale and interpreted the power demand-time curve during the mixing of carbon black with the oil-extended rubber to gage the processing quality of the masterbatch. He based a "dispersibility rating" on the time required to incorporate the carbon black to an initial stage of dispersion corresponding to a minimum in the power demand (Figure 14). Later investigators⁸⁰ have preferred to continue this test to a more advanced state of dispersion corresponding to the maximum in the power demand curve. By adopting a "mixing index" scale based on visual observations of the mix, Gale and coworkers developed a numerical index system that indicated the time to reach the minimum power demand in the Banbury cycle. The characteristic power curves for oil-extended rubber and cold SBR are illustrated in

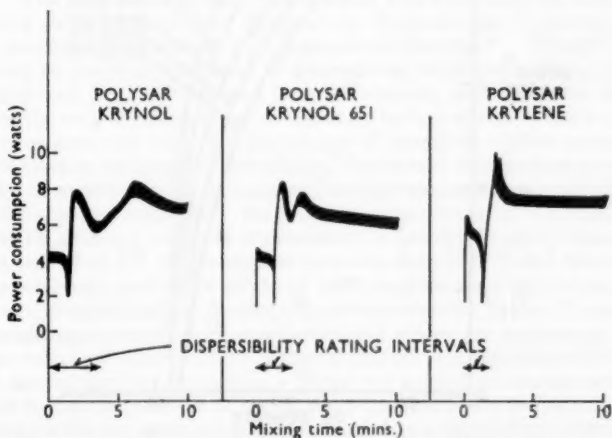


FIG. 15.—Typical Banbury power curves for mixing test. (Reference 61, Fig. 5.)

(Table IV).

Fraction	Polysar Krynol	Polysar Krynol 651	Polysar Krylene
% Below 50,000	9.1	11.3	16.1
% Below 130,000	22.0	26.5	42.9
% Above 1,000,000	29.0	14.0	3.0
% Above 1,500,000	17.2	0.3	0.0

Figure 15. Cold SBR was denoted by a mixing index of 10 and no standard oil-extended rubber has been observed to possess as good a processability as cold SBR, the nearest being that denoted by mixing indexes in the range of 8.5 to 9.5.

A comprehensive account of investigations on the cause of such behavior was reported by Buckler and Mitchell⁴². The molecular weight distribution of the base polymer showed a second peak in the region of 600,000 at low oil demands that shifted to higher molecular weights and included a larger proportion of the polymer for a polymer with a higher oil demand. The variation of molecular weight distribution with the oil demand at 60% conversion, shown in Figure 6, demonstrated why the oil demand increased and the mixing index decreased. The conversion level (Figure 5) should be limited to approximately 70%, therefore, to avoid the formation of high molecular weight branched or crosslinked polymer. A maximum limit in oil demand must be observed in order to provide satisfactory processing qualities in a tread-type recipe. This report concludes that, "as was suggested when the undesirable mixing behavior of oil-extended rubbers was first observed, a more extensive breakdown prior to the addition of carbon black improves the mixing behavior. This breakdown

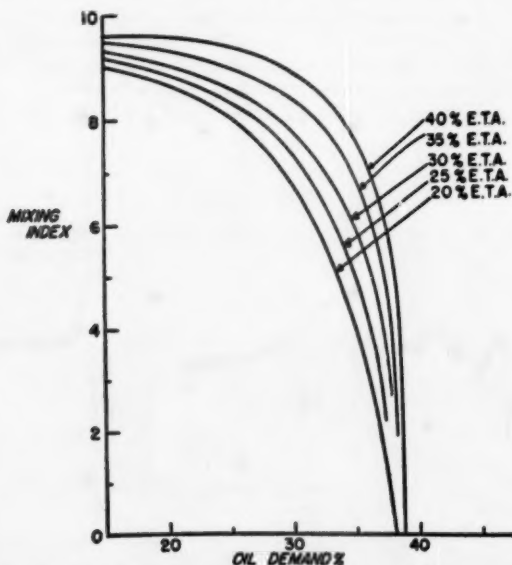


FIG. 16.—Effect of oil demand of base polymer and oil content of oil-extended rubber on mixing index value. (Reference 42, Fig. 12.)

results essentially in a reduction of oil demand of the base polymer and consequently an improvement in mixing index in line with that predicted in Figure 16".

(d) *Polymer-Extender Balance*

Reference has been made to the molecular composition of the base polymer, use of the oil demand basis for estimating a suitable softener loading, and a method for determining the carbon black level for tire tread compositions. This basic design was primarily concerned with the production of a balance between the characteristics and the amounts of the polymer and extender components in the masterbatch. The preparation of a tread-type masterbatch presented two main requirements, (a) equivalent processability and (b) equivalent vulcanizate properties. The theoretical considerations provided an expression whereby the allowable volume of diluent could be calculated from the average molecular weight of the two polymers and a selected level of crosslink density. When it is the object to add softener to a higher molecular weight low-temperature SBR to obtain the same tensile properties as a hot SBR it is only necessary to add a selected softener to the more regular cold SBR, containing a lesser amount of low molecular polymer, to equal the properties of the hot SBR containing about 30% of low molecular weight material. In order to achieve a satisfactory level of processability, it was necessary to prevent the formation of significant amounts of very high molecular weight polymer that may have an excessive degree of branched or crosslinked structures.

In mechanical goods type recipes different types of fillers are employed and other combinations of physical properties are required in service. In general, larger-particle size carbon blacks or nonblack fillers are employed and the tensile strength, etc., are at a lower level than for tread compounds. A frequent requirement in this service is that the components should provide a minimum of discoloration when light-colored vulcanizates are exposed to light and that staining of other surfaces with which the vulcanizate comes into contact, should not occur in service. This imposes a new requirement on the polymer-extender system. The polymer itself, may be stabilized with a nonstaining, nondiscoloring type of antioxidant such as Wingstay S, Polygard, etc., following the customary practice with standard SBR polymers of this type¹³. The oil^{65, 61} must be selected to maintain this level of nonstaining properties. Data presented by Buckler and Mitchell⁴² showed that the staining characteristics of the oil vary directly with the percentage of aromatic carbon atoms in the average oil molecule, or inversely with the percentage of paraffinic carbon atoms. The allowable level in staining characteristics, then would require that a relatively paraffinic, or naphthenic oil be selected but, for reasonable compatibility with a styrene-butadiene copolymer, the aromatics should not be less than 20% as measured by silica gel test. It is necessary to specify for safety reasons that the flash point⁴² of the oil should not be lower than 375° F and this value as well as a minimum molecular weight of 350⁴², applies some control on the rate of diffusion, or volatilization, for this type of extender oil (Tables XI and XIII).

In designing a general-purpose oil-extended rubber for mechanical applications, the color and color stability of the oil and the compatibility with the base polymer are primary considerations. These two properties are opposed factors as related to the composition of the oil since the first one is improved by a low aromaticity while the latter is adversely affected by a high paraffinity. Thus, it is necessary to reach a balance in the chemical nature of the oil by selecting

one that is intermediate between the paraffinic and naphthenic types and has a relatively low molecular weight so that the formation of a bloom will not occur in instances where higher quantities of less compatible materials are employed in the compounding recipes.

In such recipes, the rubber content is customarily at a lower level and, since larger quantities of various fillers and softeners are employed, there is not a critical requirement for rapid, high-shear methods of compounding nor a high tensile strength. The sequential approach to masterbatch design is not as pertinent in this case and, generally, it suffices to determine the weight loading of the particular oil which when masterbatched with the high molecular weight polymer will produce a Mooney viscosity in the range of 50 to 60. The polymer, in this case, may be a somewhat higher average molecular weight so that the oil-extended rubber may contain 50 parts of oil per hundred parts of polymer.

In many applications such as rubber soling and tile, a proportion of a high-styrene resin (bound styrene content 70%, or over) is employed²⁹ in order to confer additional hardness and flex resistance while still providing a satisfactory flow at processing temperatures for a highly-loaded compound. These are light-colored articles and special consideration must be given to the compatibility factor. Since a variable quantity of high-styrene resin may be added to such oil-extended rubbers, or additional amounts of less compatible softeners may be employed in compounding operations, care is required to select an oil that will have sufficient compatibility with the high-styrene portion to prevent the development of an objectionable bloom on the vulcanizate (so-called "bleeding out" of the softener). A relatively recent approach³⁰ to this problem is to provide a masterbatch combining a high molecular weight SBR, a high-styrene polymer and a relatively-naphthenic type oil. By designing this masterbatch to contain the maximum desired loading of high-styrene resin, and balancing the amount and type of oil employed to prevent bleeding out of the vulcanized masterbatch, one may obtain some assurance that any difficulty of this nature will be minimized in the actual compounding recipe. The assumption must be made, however, that the masterbatch will be mixed with a standard SBR and any additional softener will be of a compatible nature.

The polymer-extender balance required for oil-polymer-filler masterbatches in the mechanical goods field can not be precisely defined unless a narrow field of applications can be designated. FEF black is a general type of carbon black considered for use in such applications and loadings of 60 to 100 parts have been combined in masterbatches containing from 37.5 to 50 parts of naphthenic-type oil.

IV. SBR-MASTERBATCHED MATERIALS

A. MANUFACTURE

The manufacture of the high molecular weight SBR polymer is quite similar to that employed for standard low temperature SBR and the evolution in the type of polymerization recipes over the past ten years has followed a parallel course. The initial catalyst-activator system for polymerization consisted of a hydroperoxide type (cumene, diisopropyl benzene, paramenthane) originally activated with a sugar-iron-pyrophosphate combination then a sugar-free iron system and currently a sulfoxylate-type activator. The latter consists of ferrous sulphate complexed with a sequestering agent, sodium salt of ethylenediamine tetra-acetic acid. A typical polymerization recipe is shown in Table I. The modifier level is reduced from about 0.20 to 0.10 to allow a higher average

molecular weight polymer to be produced compared to standard cold SBR. Details of the various factors involved in the polymerization of cold SBR have been published by several authors^{10, 35} and need not be recounted here. The polymerization is carried out at 41° F, using either a rosin acid soap, or a mixed rosin fatty acid soap system as the emulsifier for a tread-type polymer. The reaction is carried to 60% conversion in about 10 hours. A conventional thiocarbamate shortstop is employed and either a staining-type stabilizer (BLE, etc.) or a nonstaining stabilizer (Polygard, etc.) may be employed depending upon the designed end use of the product.

(a) Process

There are several departures from the standard cold SBR process involved in making an oil-extended rubber³¹ that occur through the addition of the extra variable (oil) and the increase in control of the process required to ensure the correct balance of extender and polymer and to produce a uniform composition.

The extender oil is prepared as a concentrated emulsion, containing about 35% of oil, by agitating the oil at a slightly elevated temperature (140 to 150° F) with a 2 to 3% solution of a rosin soap emulsifier. Adequate care is required to obtain a stable emulsion and the oil content may be determined by ultraviolet spectrophotometric analysis.

There are two common methods of blending the oil emulsion and latex prior to coagulation (a) a batch system in which a tank is used to blend the required quantities and check the accuracy of the blend before coagulation or (b) a continuous system by which the oil and latex are pumped through flow meters to be blended in the proper proportion as they enter the coagulation vessel. A similar choice exists in the method used to add the stabilizer that is prepared as a 25% emulsion in water. Once the blend of oil emulsion, latex and stabilizer emulsion enter the coagulation vessel, with the brine/acid coagulant, the process follows the customary steps involving a holdup of the crumb in the coagulant to allow time for the soap emulsifier to be converted into the acid form, separation of the coagulated crumb on a filter followed by washing with water, subdivision of the wet crumb, drying in hot air and baling of the product. The oil-extended crumb is more subject to plastic flow during the drying stage than cold SBR types and some moderation of the air temperature may be required to prevent agglomeration in the drier. Similarly, the dry crumb shows increased flow under the baling pressure and it may be pressed under a slightly lower pressure, and temperature, than standard cold SBR.

In preparing an oil-carbon black masterbatch^{33, 34} an additional operation involves the preparation and blending of a carbon black slurry. The carbon black pellets must be disintegrated and finely-divided by mechanical action in order to prepare a dilute suspension of carbon black in water. This operation may be carried out by grinding the pellets and using colloid-type mills to disperse the carbon black in water containing 6 to 8% of an emulsifier such as a naphthalene sulphonic acid. Current methods avoid the use of emulsifier and employ a steam jet principle wherein the carbon black is exposed to a high turbulence, often produced by the sudden expansion of superheated steam through an orifice. A classification system selects the carbon black of suitable particle size and it is mixed with additional water and blended continuously with either a stream of preblended oil and latex or separate, metered streams of emulsified oil and latex. The blend is immediately coagulated in the customary brine/acid coagulant. The water content of the carbon black masterbatch

crumb is usually reduced by a mechanical method (squeeze rolls, extrusion, etc.) in order to speed up the drying cycle and reduce the amount of heat required to remove the moisture. The additional water retained by the carbon black masterbatch and its higher heat capacity make this operation an economically attractive one.

(b) Inspection Tests

The oil-extended rubber is subjected to the normal control tests⁹² applied to cold SBR which include analysis for volatile matter, ash, free soap, free organic acid and bound styrene level. The analysis for stabilizer presents a problem in the presence of oil and it is usually controlled by addition methods. The stabilizer content in the oil-extended rubber is based on the polymer content and is present to an average level of 1.25%.

The customary control method for the plasticity of the oil-extended rubber is the Mooney viscosity measurement. The Mooney viscosity (ML/4', 212° F) of the usual product is in the range of 50 to 55, according to the particular masterbatch involved, and the normal product range is plus or minus 7 points.

It is possible to achieve this mean Mooney viscosity by a combination of a high or low value for the polymer Mooney viscosity and the opposite level for oil content. An analysis for oil loading is necessary, therefore, to ensure a uniform composition. This analysis is made by a simple extraction procedure, using a 70/30 ethanol/toluene azeotrope as solvent. The azeotrope not only extracts the oil but, also, the emulsifier soap and acid contents of the masterbatch. The total extract, however, represents the total nonpolymer content and is employed as the primary control value. Since the total content of nonpolymer material (other than oil) is known by analysis or calculation, it is possible to calculate the oil loading by the following expression:

$$O = \frac{E - A}{1 - \frac{(E - A)}{(100)}}$$

where E = % ETA extract, A = nonpolymer materials normally present in the polymer (generally 6 to 7%), and O = the oil loading in parts per hundred parts of rubber.

The Mooney viscosity of the oil-extended rubber is inversely related to the ETA extract value and a linear regression equation may be determined for the particular product involved to provide a guide during production to balance the oil loading and desired Mooney viscosity of the product. Harris⁹³ determined such an expression for a 45-part oil-extended rubber and found that the Mooney viscosity of the masterbatch equalled 116.3 minus 1.65 times the per cent ETA extract. He calculated a standard deviation for this regression equation and found it to be plus or minus 2.2 Mooney points. Such correlations are most useful in development work when nonstandard polymers and extender materials are involved in the preparation of experimental masterbatches.

The physical inspection tests are carried out by compounding a 400-gram sample in a standard compounding recipe according to the procedures originally established by the Office of Rubber Reserve⁹², which includes vulcanizing test slabs at three different cure times and measuring the modulus at 300% elongation, the tensile strength and elongation at break. The compounding recipe involved varies for different types of masterbatch and between different pro-

ducers. An effort is being made to standardize the basis for selecting the recipe used for different oil-extended rubber compositions under the direction of Committee D-11 of the American Society for Testing Materials, by the British Standards Association and elsewhere. The problem is a difficult one because of the increasing variety of products that are appearing on the market from year to year.

The inspection tests applied in the case of the oil-carbon black masterbatch product are similar to those mentioned above with the added test for carbon black content⁹². It will be apparent that a suitable expression might be formed to calculate the carbon black, as well as the oil loading, on a parts-per-hundred-parts-of-polymer basis. These values are of nominal interest in quality control of the masterbatch and the ETA extract and carbon black content values provide the primary control of the composition. The inspection procedure for stress-strain properties follows the same procedure applied to an oil-extended rubber and the problem of standardizing the approach to a test recipe is much more complicated than in the case of oil-extended rubber because different types and loadings of carbon black are present in these masterbatches. This matter is receiving further attention in Committee D-11 of the ASTM at the present time.

B. COMMERCIAL PRODUCTS

Since the introduction of the first commercial products X-628 and Polysar Krynol, the number and variety of oil-extended rubbers has increased year by year. The new SBR synthetic rubber plants in Germany, Italy, England, Holland and Japan each have added their own oil-extended products to the World's markets.

The oil-extended carbon black masterbatch products have reached similar proportions although current manufacture is confined to the United States. The added factors of type and loading of carbon black adds considerably to the multitude of possible products.

An excellent list of such products was published in 1959 by Seaman and Carlton⁹⁴. Reference is directed to the current price lists in *Rubber World* or *Rubber Age* (USA), *Rubber and Plastics Age* (UK), *Kautschuk und Gummi* (Germany) or *Revue Générale du caoutchouc* (France) for periodic additions of new oil-extended products to the growing list of available types. In the United States, the ASTM assign code numbers to designate new oil-extended polymers that possess a significantly different characteristic and may be expected to occupy a definite position in this field from an end-use viewpoint.

(a) Composition

The oil-extended rubber products, basically, are butadiene-styrene copolymers of high average molecular weight (Mooney viscosity in the range of 110 to 130 [ML/4', 212° F]) blended at the latex state with a petroleum oil in the ratios of 25 to 50 parts of oil per 100 parts of polymer. The normal variables encountered in the range of SBR polymers are employed, also, in the manufacture of the high molecular weight polymer. These include: (a) emulsifier rosin or fatty acid soaps or a blend of the two materials, (b) stabilizer (staining or nonstaining), (c) coagulation system (salt-acid or glue-acid). The extender oil is a naphthenic, aromatic or highly-aromatic type with an increasing use of the more "nonstaining" oil types that are near the border region of the relatively

paraffinic and naphthenic oils in composition. Masterbatches for use in light-colored vulcanizates, or in "nonstaining" applications, would combine a nonstaining stabilizer in the polymer with a naphthenic-type oil having a low aromaticity and color.

(b) Polymer-Extender Materials

The current oil-extended products are described in Table XVII.

Included in this list are several unextended high molecular weight polymers that are available for extension by the rubber manufacturer. These allow the compounder to select special types of extender and suitable amounts for blending with the high molecular weight rubber either by a soaking treatment, by addition on the mill, or in a Banbury mixer.

Two trends are apparent in the oil-extended rubber field at the moment; the one is leading to higher loadings of oil while the other trend is to develop easy-processing masterbatches having a lower Mooney viscosity. The masterbatches containing more than 50 parts of oil are designed for the economical

TABLE XVII*

Emulsifier	Stabilizer	Coagulant	Oil type	Oil loading	Mooney viscosity	Example ^d
<i>A-1. Polymer-extender materials</i>						
FA	ST	—	—	0	120	Huls BT4
FA/RA	NS	SA	—	0	120	Kryflex 202
RA	NS	—	—	0	130	Huls BT15
RA	NS	—	—	0	150	Huls BT12
RA	NS	SA	N-NS	25	60	FR-S 173
RA	NS	SA	N	25	60	1703
RA	NS	SA	N	25	60	1773 ^a
RA	ST	SA	A	25	58	1705
RA	ST	SA	A	31	52	7701
RA	ST	—	A	31	52	FR-S 123
FA	NS	SA	N-NS	37.5	55	FR-S 178
FA	NS	GA	N	37.5	60	1708
FA	NS	GA	N	37.5	57	8200 ^a
FA/RA	NS	SA	N	37.5	55	1778
FA/RA	NS	SA	N	37.5	41	Krynox 654
FA/RA	ST	SA	A	37.5	55	1710
FA/RA	ST	SA	A	37.5	45	Krynox 653
FA/RA	ST	SA	A	37.5	52	1710C ^c
FA/RA	ST	SA	A	37.5	55	FR-S 154 ^c
FA/RA	ST	—	HA	37.5	55	1712
FA/RA	ST	SA	HA	37.5	52	1712C ^c
FA/RA	ST	—	HA	37.5	55	FR-S 155 ^c
RA	NS	SA	N	37.5	55	1707
RA	ST	SA	A	37.5	55	1709
RA	ST	SA	HA	37.5	55	1711
FA	NS	GA	N	50	55	4700
FA/RA	NS	SA	N	50	52	1713
FA/RA	NS	SA	HA	50	52	1714
FA/RA	ST	SA	HA	50	50	1714C ^c
FA/RA	ST	SA	HA	50	53	3700
FA/RA	ST	SA	HA	50	63	4701

A-2. Special extenders

Emulsifier	Stabilizer	Coagulant	Extender	Extender loading	Mooney viscosity	Example
FA/RA	NS	SA	Rosin acid	25	62	3900
FA/RA	NS	SA	?	?	50	Polymer G

TABLE XVII—Continued

Emulsifier	Stabilizer	Coagulant	Oil		Carbon black		Mooney viscosity	Example
			Type	Load- ing	Type	Load- ing		
B. Polymer-extender-pigment materials								
RA	ST	— ^b	HA	17.5 ^e	SRF	75	—	3756
FA/RA	ST	SA	N	25	HAF	50	65	1801
FA/RA	ST	SA	A	25	HAF	50	63	1803
FA/RA	ST	Acid	HA	25	HAF	50	63	8250
FA	NS	GA	N	37.5	HAF	75	58	1805
FA/RA	NS	SA	N	37.5	FEF	68.75	57	B-132
FA/RA	NS	SA	N	37.5	HAF	50	48	B-119
FA/RA	NS	SA	N	37.5	HAF	75	51	B-151
RA	NS	Acid	N	37.5	FEF	60	50	8253
RA	NS	SA	N	37.5	FEF	80	54	B-142
FA/RA	ST	SA	A	37.5	HAF	75	66	B-111
FA/RA	ST	— ^b	A	37.5	ISAF	60	61	3759
RA	ST	SA	A	37.5	ISAF	75	—	OB-111
FA	ST	GA	HA	37.5	HAF	75	56	6620
FA/RA	ST	— ^b	HA	37.5	HAF	75	62	4750
FA/RA	ST	Acid	HA	37.5	HAF	75	67	8254
FA/RA	ST	— ^b	HA	37.5	HAF	75	73	3751
FA/RA	ST	— ^b	HA	37.5	ISAF	60	65	3753
FA/RA	ST	— ^b	HA	37.5	ISAF	75	77	4752
RA	NS	SA	HA	37.5	FEF	60	—	OB-106
RA	ST	SA	HA	37.5	ISAF	75	65	8266
FA	ST	GA	HA	45 ^f	FEF	75	55	6608
FA	ST	GA	HA	45 ^f	HAF	75	55	6605
FA/RA	ST	SA	A	45 ^f	HAF	75	53	B-154
FA/RA	ST	— ^b	HA	45 ^f	HAF	75	—	9275
FA/RA	ST	— ^b	HA	45 ^f	ISAF	75	—	9250
FA	NS	— ^b	N	50	FEF	100	57	4751
FA/RA	NS	— ^b	N	50 ^g	FEF	75	—	3755
FA/RA	ST	— ^b	HA	50 ^g	HAF	75	50	4753
FA/RA	ST	— ^b	HA	50 ^g	HAF	75	54	3757
FA/RA	ST	— ^b	HA	50 ^g	ISAF	75	—	3758
FA/RA	ST	SA	HA	51.3	ISAF	82.5	—	OB-104
FA/RA	ST	SA	HA	56.8	HAF	82.5	—	OB-111

* Reference 93.

* Oil employed has low color.

* Special coagulant.

* Wingstay 100 (antioxidant-antiozonant type).

* ASTM D-1419 or manufacturer's code number.

* Process oil.

* Process oil 7.5 parts of the total oil.

* Process oil 12.5 parts of the total oil.

production of mechanical goods and mainly involve light-colored, nonstaining types of oil. The lower Mooney viscosity masterbatches are receiving favorable acceptance by the rubber manufacturer because they allow a reduction in mixing time and provide a more-rapid acceptance of fillers. The low Mooney viscosity may be obtained by either one of two methods; (a) the same oil loading and a somewhat lower molecular weight polymer or (b) a somewhat higher oil loading and the same base polymer. These factors were discussed in Section III-D-(b).

The ester-type plasticizers^{70, 71} have not been used to any significant extent in the preparation of a commercial extended product. The cost of the ester plasticizer appears to be the principle objection to their use in this field.

Only one rosin-acid extended rubber⁶⁸ has been introduced and this received considerable attention because it provided a higher tensile strength and wear

resistance than might be obtained with a petroleum oil extender. The economic factor, again, is unfavorable to the use of rosin acids and an increasing scarcity of supplies of rosin would discourage further developments along this line.

At present, a considerable speculation is being directed toward the use of stereospecific polymers as the high molecular weight polymer for extension. The first commercial product of this nature has just been announced⁹⁸. This is a stereospecific polyisoprene extended with 25 parts of oil (Shell Isoprene Rubber 500). Further developments of this type may be expected when the manufacture of *cis* 1,4 polybutadiene rubber reaches a commercial scale.

(c) *Polymer-Extender-Pigment Materials*

The current oil-extended, pigmented masterbatch products are described in Table XVII. The major class of products involves the various types of furnace blacks in masterbatches designed for use in tire compounds. These materials initially employed HAF carbon black and progress has led to the use of finer furnace-type carbons (ISAF and SAF). A gradual and balanced increase in the carbon black and oil loadings is taking place as the tire compounder obtains a greater familiarity with the excellent balance of processability and wear resistance that is provided by the more recent oil-extended rubbers in combination with the nondispersant, "jet" process for latex-blending of the carbon black.

The recent developments towards a lower Mooney viscosity product in the oil-extended rubber field may be expected to include oil-extended carbon black masterbatch products in the near future. Other developments will undoubtedly include the newer furnace-types of carbon black which have been designated by the codes HAFF, ISFF, and SAFF⁹⁴. The more-reinforcing grade (SAFF) has been mentioned as one that is rather difficult to disperse by dry-mixing techniques and, on this basis, it may be of considerable interest when employed in an oil-extended carbon black masterbatch.

The extender-pigment masterbatch products designed for use in the mechanical goods field have used the FEF grade of carbon black in many cases. This tendency probably reflects the need for a significant pigment contribution to the reinforcement potential of the oil-extended rubber. In at least one instance, an SRF black masterbatch has been produced commercially but this is a border-line case where an SBR-1500 type was extended with 17.5 parts of a processing aid.

While no commercial products have been introduced that contain a white pigment it might be expected that reinforcing types of silica and alumina would see some use in a masterbatch. The economic balance involved in the production and use of such a masterbatch is not clear at the moment.

(d) *Special Types*

The use of the oil-extension principle offers interesting possibilities in other fields of polymer applications. One of these fields concerns the production of footwear soling vulcanizates produced, either in a solid or cellular form, from a blend of SBR and the so-called high-styrene resin⁹⁹. The resin portion contributes stiffness and wear resistance to the vulcanized blend. A new product⁹⁰, KO-50, has appeared for these uses that consists of a latex blend of 50% of high styrene resin and a non-staining, oil-extended rubber. This polymer-oil-polymer masterbatch opens a new field for oil-extended rubbers and other combinations of such ingredients may be expected to appear on the market.

V. TECHNOLOGY

A. COMPOUNDING PRINCIPLES

The basic approach to recipes for compounding oil-extended rubbers is still not clear even after ten years of commercial application¹⁰. Since the product contains approximately one part of oil and two parts of polymer, there is a tendency on the part of the rubber compounder to consider it as a softener masterbatch and to base the recipe on a hundred parts rubber in the customary manner, i.e., 100 plus 37.5 parts of oil or 137.5 parts of masterbatch. The synthetic rubber producer, however, is aware that he is producing a rubber product and that it is competing with other rubbers on an equal weight basis. The polymer, itself, was designed from this point of view and it is logical to base the compounding recipe on 100 parts of oil-extended rubber. The two methods are illustrated for a tread-type recipe in Table XVIII. It will be clear to a rubber compounder that in recipe (a) all of the ingredients, except the carbon black and process aid, are involved in either the vulcanization or the stabilization of the polymer. The carbon black level has been selected to be 45% by weight on the masterbatch, rather than the polymer content, in recognition of the oil-extension principle.

TABLE XVIII
COMMERCIAL TREAD-TYPE RECIPES FOR OIL-EXTENDED
RUBBER AND COLD SBR*

Recipe	a	b	c
Oil-extended rubber (1710-type)	137.5	100	—
Cold SBR (1500-type)	—	—	100
ISAF carbon black	61.9	45	45
Zinc oxide	4.15	3	3
Stearic acid	2.05	1.5	1.5
Flexamine	1.4	1	1
Liquid asphalt	2.75	2	7
Santocure	0.95	0.7	1
Diphenyl guanidine	0.2	0.14	0.20
Sulfur	1.75	1.27	1.75

* Reference 61, Table V, addition (a).

When the recipe is based on 100 parts of masterbatch (Recipe b) the similarity between the recipes for oil-extended and cold SBR rubbers becomes more apparent, principally because this is a more familiar form of recipe. There are two differences in the Recipes (b) and (c), the accelerator and sulfur loadings but only to the degree that the loadings in (b) are based on the polymer content of the oil-extended rubber, i.e., on this basis they are identical. This procedure recognizes the fact that the sulfur does not react with the petroleum oil molecules during vulcanization. Some compounders still hold that the petroleum oil acts as any other diluent material and so reduces the sulfur concentration in the mixed compound. Others have argued that the oil facilitates the distribution and dispersion of the sulfur and accelerators throughout the compound and, thus, has a neutral overall effect.

It would appear very reasonable to accept the idea that oil-extended rubbers are a new type of rubber and that somewhat different compounding and processing practices may need to be followed. If this approach is accepted there will be marked similarities between the methods followed for oil-extended and SBR

rubbers. The oil-extended rubber requires the same loading of reinforcing carbon blacks as cold rubber and the sulfur and accelerator loadings are the same but now are based only on the polymer content. The oil-extended rubber provides a more thermoplastic compound than does cold SBR and only a very small quantity of process oil⁷⁴ is required, mainly to assist in "cleaning up" the last traces of the dry fillers in the mixing equipment. The "heat-softening" of the early types of oil-extended rubbers, experienced during the drying or storage of the rubber, has led to the impression that a higher loading of antioxidant and antiozonant are required in oil-extended rubber compounds for equivalent age and weather resistance. There does not appear to be any real basis for this belief with respect to the current masterbatch materials. The more aromatic oils are known to be more prone to oxidation and, hence, basing the antioxidant content on the masterbatch instead of the polymer content may not be amiss.

This opinion is provided by reasoning similar to that which suggests that high sulfur and/or accelerator loadings are required for oil-extended rubbers because the modulus and hardness values are lower than for similar SBR-1500

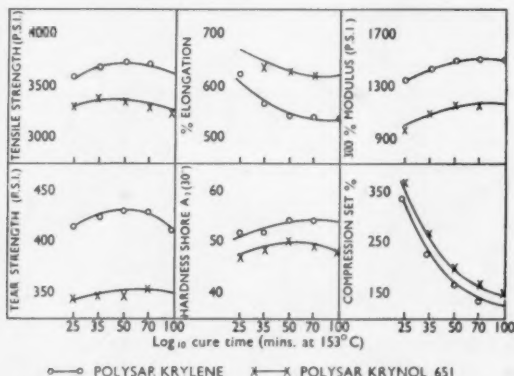


Fig. 17.—Comparison of physical properties of oil-extended rubber and cold SBR tread vulcanizates. (Recipe—Table XVIII.) (Reference 61, Fig. 14.)

vulcanizates. The lower level of these properties does not indicate, necessarily, a lower rate of cure for the oil-extended compound. The physical properties are quite typical of the new product, an oil-extended rubber in which oil has been blended with a higher molecular weight polymer to match the effect of the 30% of low molecular weight polymer in hot SBR.

In compounds reinforced with furnace carbon blacks of fine particle size the hardness and modulus of the oil-extended rubbers (Figure 17) are only moderately lower than those of cold SBR. In compounds containing coarse carbon blacks, however, the difference may be quite large and recipe changes may be required to match the physical properties provided by cold SBR. These changes might involve substituting a carbon black of finer particle size, or higher structure, increasing the quantity of carbon black and/or increasing the quantity of curatives. These are well-known practices employed for compounding a new type of rubber to produce certain properties in the vulcanizate. Similar adjustments may be necessary in the use of white fillers. Actually,

this characteristic behavior suggests compound changes that will take full advantage of the potential ability of the higher molecular weight polymer contained in the masterbatch. A further economy is obtained when it is desired to increase the hardness or modulus level by adding more filler. This point was emphasized by Gale⁶¹ and by Dorko⁹⁷.

The effect of sulfur and the customary accelerators on the vulcanization of oil-extended rubbers is very similar to that for other SBR types when the amounts are based on the polymer content in both instances. The oil content tends to provide more uniform distribution of the curatives throughout the compound. The mixing temperatures are generally lower for equal volume additions of pigments and somewhat longer scorch times may be encountered in such cases, particularly with masterbatches containing aromatic-type oils. The rate of vulcanization, however, is at least equal to that of a corresponding SBR compound as judged by the cure time required to reach an optimum balance of properties. This, of course, does not mean the identical level of hardness or modulus but the same state-of-cure in the polymer component, defined as an equal crosslink density. Ebonites of excellent hardness and flexibility may be obtained with an oil-extended rubber and, in this instance, it is advisable to employ slightly higher levels of sulfur than for an SBR polymer because the percentage concentration of sulfur in the compound will have an influence when the ultimate crosslink density is required, particularly, if this is to be accomplished in the same time as observed with an SBR compound.

When additional softeners are to be added to an oil-extended rubber compound to lower the hardness, increase tack, affect the flex-crack resistance, etc., it will be observed that such materials produce a greater effect than a similar loading in an SBR compound and, indeed, a slightly higher ratio of filler to softener may be employed to lower the rubber content and maintain an equal level of hardness, etc.

When appreciable quantities of softener are to be used, for instance to produce sponge compounds, it is well to select a softener that is compatible with the oil present in the oil-extended rubber so that no problems will be encountered through bleeding of softener or a formation of bloom on the surface. Thus, high loadings of relatively paraffinic-type oils should be used with caution and it is preferable to use a blend of softeners that match the aromaticity of the oil-extender in the rubber. These comments are more pertinent if a high-styrene resin is present in the recipe since the compatibility of paraffinic-type oils is lower with this polymeric material than in the case of polymers having a lower bound styrene content.

The polymer-extender-carbon black masterbatches should be viewed as masterbatches of oil-extended rubber and carbon black. Similarly to the current practice with SBR black masterbatches, a certain quantity of the oil present acts as a process aid. This is in recognition of the fact that, by latex compounding, the polymer has not undergone a breakdown effect such as would be the case in dry-mixing the equivalent amount of carbon black in an SBR product by mechanical means. The polymer hydrocarbon, therefore, possesses the original level of molecular weight with corresponding high strength and elasticity characteristics. The principle objective in carbon black masterbatching is to provide an initial high level of carbon black dispersion and, thus, only require a brief mixing time to add the remaining compounding ingredients and reach a suitable plasticity level for the shaping operations that are to follow. The unmasticated polymer can absorb somewhat more than the loading of

process oil that is added during dry-mix operations and this quantity of oil may be added to the masterbatch at the latex blending stage.

In designing a compounding recipe for a carbon black masterbatch of an oil-extended rubber, it is most convenient to consider the masterbatch to be composed of "X" parts of carbon black per 100 parts of oil-extended rubber. The trend in the last few years has been to include additional oil in the masterbatch as a process aid. This practice makes it more necessary to identify the quantity of oil that is required by the high molecular weight polymer according to the oil-extension principle. Any departure from the design basis that employed a weight of HAF carbon black equal to half the weight of polymer plus oil may require that a new balance be found between the processing and physical properties of the compound. Such adjustment may be performed most easily by changes in the oil and/or carbon black contents with a knowledge of the oil demand of the polymer contained in the masterbatch. Thus, the compounding recipe may be based on 100 parts of oil-extended rubber to facilitate the design (Table XIX). Examples of this method are given by Drogin⁷⁴.

TABLE XIX
TREAD RECIPE DESIGN FOR CARBON BLACK MASTERBATCHES OF
OIL-EXTENDED POLYMERS
(Original)

(1) Polymer	100	Oil-extended rubber	100
Highly-aromatic oil	37.5	HAF carbon black	54.6
HAF carbon black	75		
	212.5		
(2) Polymer	100	Oil-extended rubber	100
Highly-aromatic oil	45	HAF carbon black	54.6
HAF carbon black	75	Process oil	5.5
	220		
(3) Polymer	100	Oil-extended rubber	100
Highly-aromatic oil	50	HAF carbon black	54.6
HAF carbon black	75	Process oil	9.1
	225		

(2) Contains 7.5 parts of oil as process aid.

(3) Contains 12.5 parts of oil as process aid.

B. MANUFACTURING PRACTICES

The early types of oil-extended rubber showed characteristics in factory operations that were different from those observed with low temperature SBR polymers. Harrington¹¹ and Weinstock⁷⁷ described these effects and indicated measures that were taken to compensate for such behavior. Their remarks dealt with the use of a 45-part oil masterbatch in the factory production of tire treads. The points discussed were common to all levels of oil extension in the first production stage and appear to be partly due to the nature of the high molecular weight polymer and, partly, a result of variations in the Mooney viscosity between lots of the same material. The difficulties, indeed, were quite similar to those encountered in the early types of GR-S. Fortunately, rapid progress was made in adjusting the performance of the oil-extended rubber through a better knowledge of the factors involved^{41, 42, 44, 60}. The problems

were eased, also by the ability to blend the oil-extended rubber with low temperature SBR and thus progressively approach a usage of 100% oil-extended rubber as satisfactory solutions were obtained for the various processing difficulties.

The early products tended to discharge from the Banbury mixer after the carbon black addition stage as a mass of crumbs. This gave difficulty at the sheet-off mill because the mass did not pass through the rolls fast enough to accommodate the rate of discharge. This masterbatch had a higher Mooney viscosity than a comparable cold SBR mix by some 30 to 40 points and it was necessary to pass it through the rolls of the mill at least twice to form a coherent sheet. The Mooney viscosity of the oil-extended rubber mix¹¹ was reported to decrease progressively at each stage of mastication and did not achieve an equilibrium value until the final extrusion stage.

The highly elastic nature of the compounded material was evidenced by a low green-strength and difficulty in preparing adequate tread splices that would resist the stresses introduced by the bagging operation. It was an early practice to use a natural rubber gum strip to provide adequate adhesion at the splice area⁷⁷. The opening of tread splices was a difficult problem and it was beneficial to use a shallower splice cut, splicing cements and to hold the splice area under pressure to allow some relaxation of stress to take place. There is no doubt that the introduction of the Bag-O-Matic curing press, which eliminated the need to deform the green tire to insert a curing bag, did much to resolve this problem in tread splicing.

These processing problems could be overcome by a longer mastication time or by using chemical peptizers¹¹ (Xylyl mercaptan) to accelerate the rate of breakdown. Parallel developments in the manufacture of the oil-extended polymer and in factory operation led to a progressive improvement in these factors.

The same type of processing difficulties were encountered to a lesser degree when oil-extended rubber tread compounds were prepared in a high-pressure, high-speed Banbury cycle some five years later. This spurred the development of easier-processing oil-extended rubbers and resulted in the adoption of methods to evaluate mixing characteristics^{61, 80} which are used to control the uniformity of the product. It may be stated, that the behavior of oil-extended rubbers in factory operations is now quite satisfactory and indeed, superior to that of cold SBR in several details.

The current mixing practices for large-volume tread compounds employ high-speed, high-pressure Banbury cycles. A typical No. 11 Banbury cycle for a tread recipe is given as:

A. Oil-extended rubber	0 mins.
HAF carbon black	$\frac{1}{2}$ mins.
Process oil	2 mins.
Dump	3 mins.
B. Masterbatch as above	0 mins.
Vulcanizing ingredients	$\frac{1}{2}$ mins.
Dump	1 $\frac{1}{2}$ mins.
C. Vulcanizate properties	

There are numerous references to the effect on various vulcanizate properties of various types and loadings of oil^{41, 60, 82}, carbon black^{11, 60, 96}, white fillers^{11, 63, 96}, and accelerators^{60, 96}. An excellent summary⁹⁶ of the compound-

ing practices applied to oil-extended rubbers has recently been published. It is desirable to consider oil-extended rubbers as a class of new polymers and to consider the properties of their vulcanizates on this basis. Rather than make a detailed comparison of each property to that of some earlier polymer, this section will endeavor to describe the balance of properties and the effect of certain basic variables.

The basic masterbatch design implies that the polymer composition and the loading of extender have been balanced and complement each other. The parent, unextended polymer is an SBR-1500 having a high molecular weight. The extended rubbers having 25, 37.5, 50, etc., parts of extender per 100 parts of polymer form a sequence of products; all have a Mooney viscosity in the range of 50 to 60 and they differ only in their content of polymer hydrocarbon. Thus (Figure 18), the tensile strength in a 45-part ISAF carbon black compound varies from 4000 psi for cold SBR to 2800 psi for a 50-part oil masterbatch. The tensile strength decreases in proportion to the percentage of polymer in the oil-extended rubber (Figure 18). Similarly, the elongation at break increases, and the hardness, modulus and tear strength decrease with an increase in oil demand of the polymer. At an extender loading of 50 parts the tensile

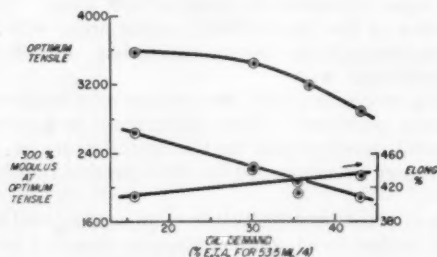


Fig. 18.—Variation in Physical Properties of a 50-part HAF tread vulcanizate for oil-extended rubbers of different oil demand. (Reference 42, Fig. 10.)

strength is approximately equivalent to that of a hot SBR vulcanizate but the other stress-strain properties are similar to those of a softer, more-extensible vulcanizate. Harrington¹¹ presented stress-strain curves comparing 50 parts loadings of EPC black in hot SBR with HAF black in oil-extended rubber (45 parts oil). The stress-strain curves were almost identical at both 77° F and 212° F. The oil-extended vulcanizates containing EPC black had a considerably lower modulus and higher elongation at break at both of these test temperatures. This trend is a characteristic of oil-extended rubbers and their stress-strain properties are similar to those of hot SBR for high structure fillers but, at the same loading, the vulcanizates become progressively softer than those of SBR the lower the oil capacity of the filler.

The polymer hydrocarbon content of the oil-extended rubbers range from 65 to 80% and, as might be expected, the addition of further softener has a proportionately larger effect than in SBR compounds. In the case of furnace black compounds, the hardness and modulus may be held relatively constant by adding the same amount of carbon black based on the extra softener as that based on the oil-extended rubber. When coarser types of carbon black or white fillers are involved, higher quantities of filler will be needed to adjust these

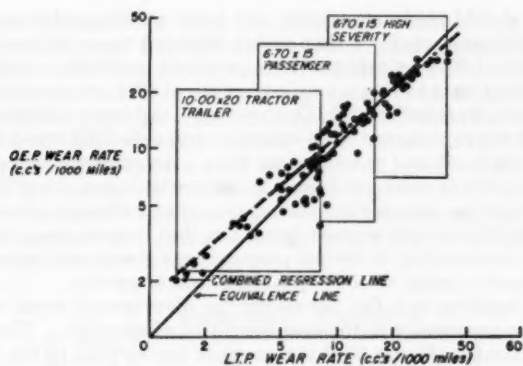


FIG. 19.—Comparison of road wear of oil-extended rubber and cold SBR type tread vulcanizates. (Reference 98, Fig. 9.)

properties for an additional amount of softener in oil-extended rubber compounds. Harrington¹¹ showed data to illustrate these effects.

The stress-strain properties are affected in the normal manner by an increase in the sulfur or accelerator levels¹¹. While the hardness or modulus of the vulcanizate may be increased by such an increase of curatives, it should be understood that the normal degree of crosslink density in the polymer is achieved by employing the same level of curatives, based on polymer content, as for a SBR compound, i.e., the loading of curatives for oil-extended rubber should be about 20% less than employed with SBR. Increased levels of accelerator or sulfur, will decrease the flex life and heat build-up of the vulcanizate without a significant effect upon its wear resistance.

The lower tensile strength of oil-extended vulcanizates is characteristic and

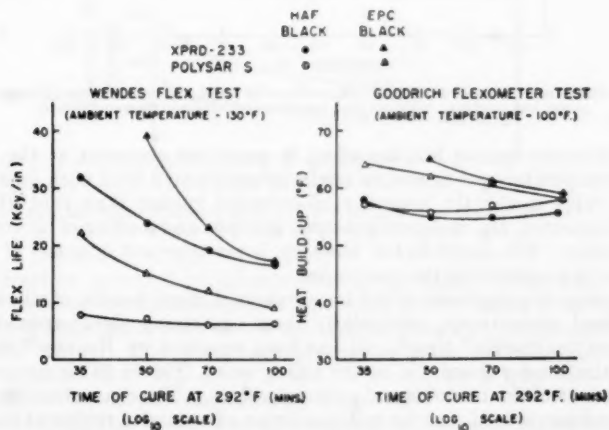


FIG. 20.—Flex-hysteresis properties of XPRD 233 (oil-extended rubber) and polysar S tread vulcanizates. (Reference 11, Fig. 6.)

this property should not be associated with lower quality performance. It has been amply demonstrated^{11, 98} that an oil-extended tread vulcanizate with a tensile strength of 3000 psi will provide equivalent tread wear to that of a cold SBR tread vulcanizate having a tensile strength of 4000 psi or over (Figure 19).

Harrington¹¹, Buckler⁴², Gale⁶¹, Dannenberg⁸⁴, and many other workers have compared the wear resistance of oil-extended and cold SBR tread vulcanizates by road tests on truck and passenger car tires. An extensive comparison over a range in severity of wear conditions is summarized in a paper by Gelinas⁹⁸. He reported that the oil-extended rubber vulcanizate showed somewhat higher wear than cold SBR at low severity levels but that it gave comparable wear at the severity corresponding to normal passenger car service and actually showed better performance under more severe conditions of service.

The heat build-up and flex life values for oil-extended tread vulcanizates are reported to be superior to those of hot SBR¹¹ (Figure 20). The power loss of such vulcanizates (Figure 21)⁹⁹ is somewhat higher than in the case of cold

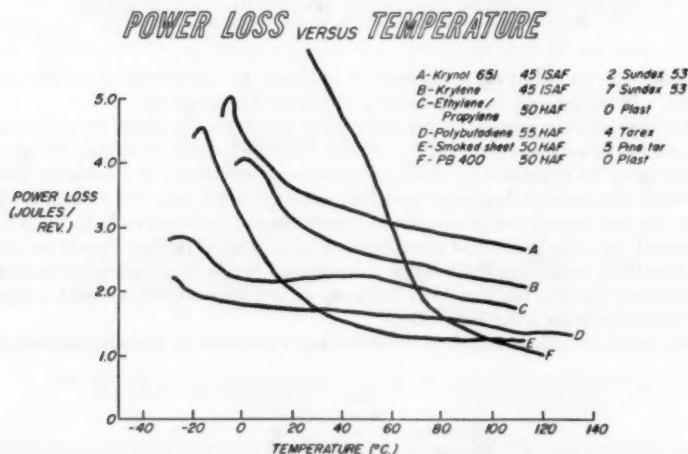


FIG. 21.—Power loss measured at various temperatures for tread type vulcanizates (Dunlop rotary power loss machine—constant load conditions) (Reference 99, unpublished)

SBR in dynamic service but the effect is much less apparent at the normal running temperatures of tires than might be anticipated from such data. The rebound value is slightly lower for oil-extended rubber than cold SBR⁶² as might be expected, and is dependent upon the type and loading of oil employed in the rubber. The major factor, however, is the type and quantity of carbon black that is employed in the compound.

Advantage is being taken of the lower rebound characteristic of oil-extended rubber tread vulcanizates, particularly those containing highly-aromatic oils, to produce "quite-ride" tires⁹⁸. It has been reported by Rooney¹⁰⁰ that the effect of the tread vulcanizate on the riding index (Figure 23) is proportional to the product of the modulus and rebound values. The characteristics shown by butyl rubber, indeed, may be matched by an oil-extended rubber of this type.

The aging characteristics of oil-extended rubber vulcanizates were reported by Harrington¹¹ (Figure 22) to be equivalent to those of a hot SBR vulcanizate.

Mitchell¹⁵ showed that even when the oil-extended rubber has undergone a degree of "heat-softening" through the presence of trace metals, the vulcanizate properties (Table XIII) are not appreciably affected by measurable changes in the viscosity of the base polymer. The presence of significant amounts of these heavy metals might be expected to have an adverse effect on the aging characteristics of the vulcanized rubber. The oil-extended SBR polymer, however, is reported to have a good resistance to aging conditions, such as heated air. The increase in crosslink density that normally occurs in SBR vulcanizates under such conditions apparently is counteracted by the presence of the oil and, as a net result, the rate of stiffening of the vulcanizate is less than observed in cold rubber vulcanizates.

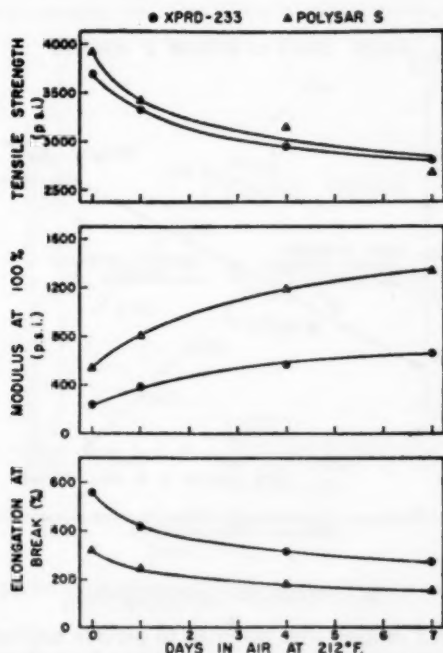


Fig. 22.—Effect of heating in air at 212° F on the stress-strain properties of tread vulcanizates. (Reference 11, Fig. 4.)

The traction provided by oil-extended rubber tread vulcanizates on dry, wet and snow-covered road surfaces was reported by Grace¹⁰¹ to be better than that of hot SBR or cold SBR tread compositions and quite similar to that of natural rubber. The advantage in traction obtained with oil-extended rubbers suggests that this effect is also improved by a soft, low-resilience vulcanizate in the manner suggested by Figure 23.

The relatively high amount of oil present in an oil-extended rubber results in effects on the vulcanizate properties that are related to the properties of the oil (Table XI). Weinstock⁶² describes the significant contributions of the oil

as determined by laboratory and factory tests (Table XV). The flexibility at low temperatures was found to be related to the type of oil employed and an aromatic-type oil gave poorer low temperature properties than either the relatively naphthenic or paraffinic oils. The aromatic oils were said to be more volatile at elevated temperatures than either the naphthenic or paraffinic-type oils and a minimum molecular weight level of 350 was suggested for extender oils. Weinstock reported that, at equal volume loadings, the composition of the oil had little effect upon the stress-strain properties or rebound value of factory-mixed compounds either at room temperature or at 205° F. He presented data indicating that the aging characteristics and road wear (Table XII) of oil-extended rubber vulcanizates was not significantly affected by the type of extender oil.

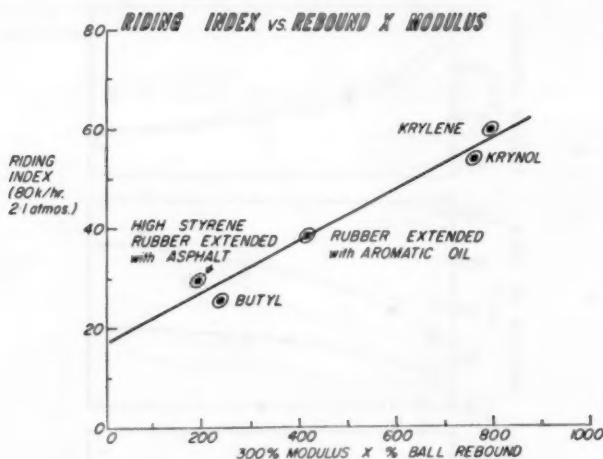


FIG. 23.—Relation of modulus and resilience to riding characteristics (Reference 100, unpublished).

D. COMMERCIAL APPLICATIONS

The oil-extended rubbers were designed to provide satisfactory tire tread vulcanizates and the larger volume of these rubbers is employed in the manufacture of automobile tire treads and sidewall compositions, in tire carcass stocks and the manufacture of camelback and tire repair materials. The performance of the oil-extended rubber in these products has been outstanding and, in North America, passenger car tires contain nearly 100% SBR rubber of which the oil-extended types account for nearly 50% of the total. A considerable proportion of oil-extended rubber is being employed in truck tire treads where a significant amount is employed in sizes up to 10.00 × 20.

Large quantities of oil-extended rubbers are being employed in other transportation uses, such as tractor tires, transmission belts, V-belts, solid industrial tires and conveyor belts as well as in accessory items such as mud flaps, torsion couplings, coolant hose, bearing pads, etc.

The wide acceptance of oil-extended rubber vulcanizates for dynamic services in the transportation field has been paralleled by extensive applications in the mechanical goods field. Here, the 50-part oil masterbatches provide a desirable easy-processing and economical material for both black and light-colored articles. The application of oil-extended rubbers in sponge underlay and cellular rubber compositions has reached a high-volume level because the soft and plastic nature of such compounds leads to a lower density and a more uniform expansion of sponge compositions. The ability to provide high extrusion rates with lower shrinkage levels has led to an extensive use of these rubbers in extruded goods. Applications of these rubbers in complex extruded shapes for weather-stripping, gaskets and seals have reached high proportions and the excellent mould flow of its compounds, combined with a low scorch characteristic, has allowed extensive use in multicavity compression and injection mold-

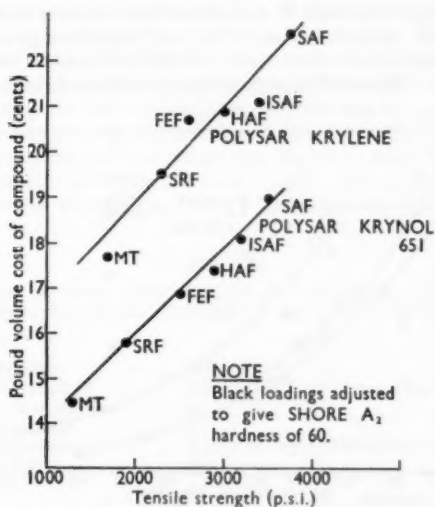


FIG. 24.—Volume cost of oil-extended rubber and cold SBR carbon black vulcanizates at equivalent hardness. (Reference 61, Fig. 11.)

ing operations. These same characteristics have led to extensive development of oil-extended rubber compounds for use in molded-on soling operations and such compounds are particularly suited to the manufacture of footwear in low-pressure, automatic molding machines. The use of these rubbers in high-styrene soling compositions represents a large proportion of the SBR consumed in these products and its flow properties and capacity for white fillers provide advantages in the production of cellular sponge sheeting either by compression molding operations or the Roto-cure continuous vulcanization process.

A typical compounding recipe for many of these applications was given by Gale⁶¹ and Dorko⁹⁷. Figure 24 compares the volume cost of cold SBR and oil-extended rubber vulcanizates with various carbon blacks on a basis of equal hardness.

VI. OTHER BUTADIENE RUBBERS

The oil-extension principle is particularly suitable when applied to butadiene copolymers because the variety of chain structures and the range in molecular weights that are available in this polymerization system³³. The process of adding a low molecular weight oil to a high average molecular weight rubber that is adequately reinforced only by the addition of fine structure-type fillers is one that can be applied quite widely in the rubber field. The production of adequate physical properties by a balanced addition of softener and filler however, must be accompanied by a suitable level of processability at the same loading of extender.

A. ALFIN-CATALYST POLYMERS

The Alfin catalyst¹⁰² will polymerize butadiene or butadiene-styrene mixtures, at an extremely high rate in a hydrocarbon medium to produce a linear, very high molecular weight rubber. The polybutadiene polymer is reported to have molecular weights in the region of 10,000,000 and to be very tough and difficult to process. Stewart⁴⁰ reported that the Alfin polybutadiene has a very

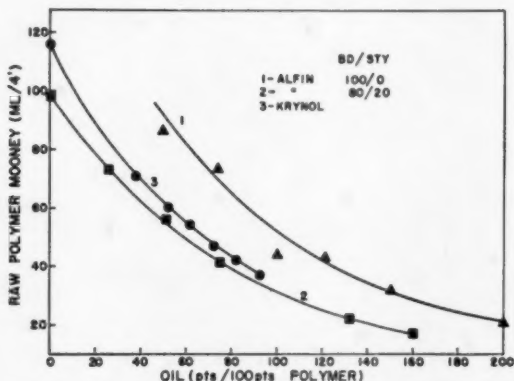


Fig. 25.—Oil-extension of Alfin rubbers (Reference 104, revised).

high elasticity and viscosity that gives a rough and irregular extruded shape and is difficult to mill resulting in a lacy sheet. This polybutadiene is said to give poor physical properties at low plasticizer loadings because of the difficulty in properly dispersing the carbon black. Morton¹⁰² reported that, with properly dispersed carbon black and oil, good tensile strengths are obtained for Alfin polybutadiene with high oil loadings. The processability of the Alfin rubber can be improved by copolymerizing styrene with the butadiene¹⁰³ but, even so, the processability was found to be much inferior to that of cold SBR polymers.

In view of these findings, it is not surprising that the oil extension principle was applied in an attempt to improve the processing qualities of Alfin polymers. Stewart⁴⁰ reported that certain softeners may be present during Alfin polymerization, although some increase was observed in the catalyst requirement. Since the polymerization is carried out in a hydrocarbon medium, it would be possible, also, to add the softener to the swollen mass at the end of polymeriza-

tion. Either of these methods would provide a way of dispersing the softener throughout the high molecular weight polymer.

Stewart and Williams⁴⁰ examined Alfin butadiene and butadiene-styrene copolymers extended with a naphthenic type oil (Circosol 2XH) and found that the milling behavior of polybutadiene was somewhat improved by the addition of oil. The copolymerization with styrene produced a more-pronounced reduction in the milling time required to produce a hole-free sheet. However, even with a bound styrene content of 28%, and additions of 30 to 40 parts of oil, it was found that the milling behavior was much poorer than that of cold SBR. Figure 25 compares the effect of oil loading on the Mooney viscosity of the raw polymer¹⁰⁴ for Alfin rubber and the SBR high molecular weight polymer. The Alfin polybutadiene polymer required an oil loading of about 100 parts to reduce the Mooney viscosity to a value of 50 but the masterbatch could not be handled on a mill. It was possible to compound it in an internal mixer when a rather crumbly mix was obtained with carbon black. An 80/20 butadiene/styrene copolymer polymerized in the Alfin system had a similar Mooney viscosity at various loadings of oil as a high molecular weight SBR polymer prepared in the emulsion system. In a 50-part HAF carbon black compound, however, the Mooney viscosity of the Alfin polymer was some 20 points higher than the SBR compound at an oil loading of 45 parts. The Alfin-oil masterbatch had to be compounded in a laboratory Banbury mixer¹⁰⁵ because of the very long times required to compound it on a mill. The combined effect of the oil loading and styrene content gave a very thermoplastic mix and it formed a

TABLE XX

PHYSICAL PROPERTIES OF ALFIN POLYMERS; 60 PARTS CIRCOSOL 2XH AND 50 PARTS OF HAF CARBON BLACK PER HUNDRED PARTS OF POLYMER PLUS OIL*

Parts						
	Polymer	100				
	Philblack O	50/100 parts oil plus rubber				
	Stearic acid	2				
	Zinc oxide	5				
	Santocure	1.25/100 parts rubber only				
	Sulfur	2.0				
Polymer No.	Charge ratio	Cure, min at 292° F	Tensile, lb./sq in.	Modulus		Elongation, %
				100%, lb./sq in.	300%, lb./sq in.	
Oil added after polymerization						
64A	100/0	50	2865	200	1490	460
64B	100/0	50	2040	—	680	560
94	100/0	15	1745	—	—	210
82	90/10	50	2260	—	620	650
80	80/20	50	2700	—	1050	540
81	70/30	100	2210	—	690	600
Oil added before polymerization						
70	100/0	50	1610	290	800	550
96	100/0	25	2410	—	1090	500
85	90/10	35	1630	—	490	640
87	80/20	50	2670	—	430	710
89	70/30	50	1845	—	360	730
130	80/20	35	2685	—	890	610

* Reference 40, Tables XX and XXII.

solid mass around the Banbury rotors and had to be cut free in order to discharge the compound. In spite of this high thermoplasticity, the rate of extrusion through a Garvey die was only about 50% of that obtained for the oil-extended SBR polymer having the same Mooney viscosity. The extremely high elasticity of the Alfin polymer appeared to be retained even at oil loadings above 100 parts of Circosol 2XH, but the viscosity was too low to provide an adequate processability. An informative discussion of such processing behavior is provided by Gessler¹⁰⁶.

The modulus of a 50-part HAF treadstock of Alfin rubber is relatively low despite the high average molecular weight. It is reduced quite sharply by additions of oil and does not respond to changes in the bound styrene level (Table XX). The micro tensile strength of such vulcanizates was in the range of 4000 psi for Alfin polybutadiene and varied directly as the polymer content in oil-extended compositions. This relationship (Figure 26) had a slope very similar to that of a high molecular weight SBR polymer. At each oil loading the tensile strength was significantly decreased by the copolymerization with styrene thus detracting from this method for improving the processability. The Alfin-polybutadiene¹⁰⁸ has a higher content of *trans* 1,4 and 1,2 structures than cold SBR and the relatively poor low temperature characteristics are adversely affected by copolymerization with styrene.

The oil-extension principle was applied to two Alfin butadiene-styrene copolymers⁴⁰. The styrene level and oil loading were selected to provide a compromise in the balance of processability and physical properties. The modulus at 300% elongation in the 50% HAF treadstock was around 750 psi while the tensile strength was about 2700 psi. These values confirm the conclusion reached by Einhorn³⁸ that there is no significant advantage to be gained by addition of oil to an extremely high molecular weight polymer.

In order to complete the examination¹⁰⁵, an Alfin copolymer was master-batched with oil and compounded in a tread recipe in a factory Banbury mixer. The compounded polymer was very thermoplastic, could not easily be strip-fed or cut from mill rolls. It was too soft to provide satisfactory extrusion characteristics and entrapped large volumes of air. Passenger car tires were built using this Alfin tread compound and the tread wear was measured in the course of normal, everyday usage. The wear rating was only 66% of that measured for an oil-extended SBR tread compound. This may be compared to a rating of 117 relative to SBR as reported for an unextended 80/20 butadiene/styrene Alfin copolymer¹⁰⁸.

It may be concluded that the elasticity of Alfin butadiene or butadiene/styrene copolymers is so high that if sufficient oil were added to provide reasonable level of processability the viscous properties would be reduced below a satisfactory level and the amount of oil required would be much in excess of what could be tolerated to obtain a suitable level of physical properties.

B. ZIEGLER-CATALYST POLYMERS

In the last five years there has been a vast expenditure of effort made to develop stereoregular polymers prepared by Ziegler-Natta-type catalysts¹⁰⁷ in hydrocarbon media. Unlike the Alfin catalyst, this system provides a very high *cis* 1,4 chain structure in polybutadiene and also results in a high average molecular weight polymer. While it is reported that butadiene/styrene copolymers are possible by this catalyst system, the major emphasis has been placed on the polybutadiene polymer¹⁰⁸ and the current state of knowledge

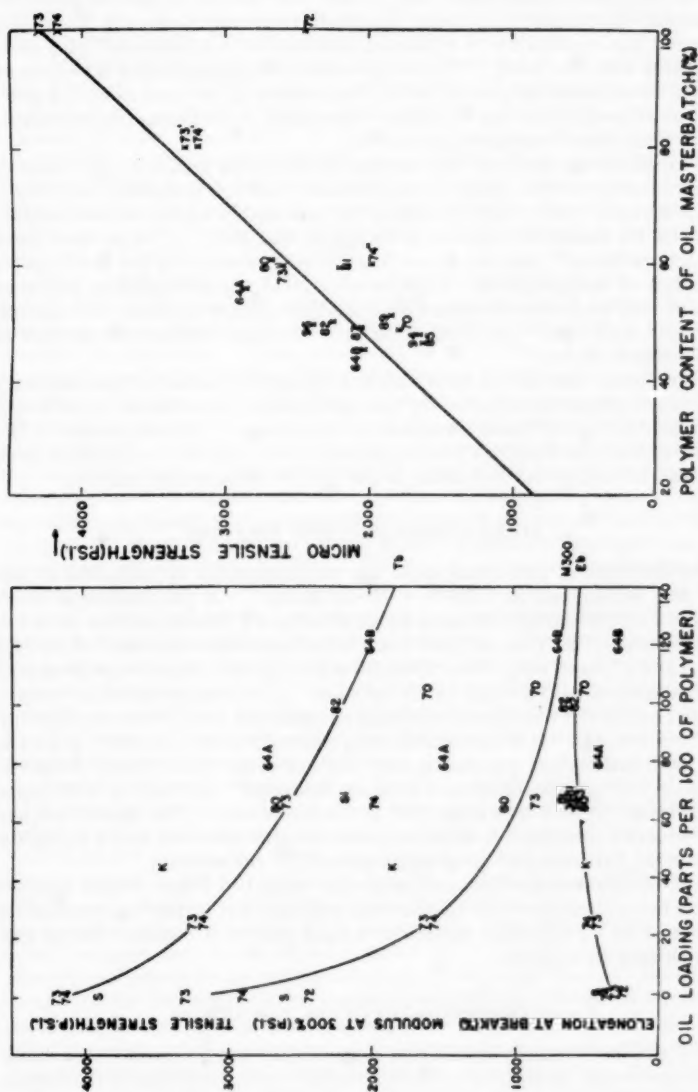


Fig. 26.—Physical properties of Alfin butadiene-styrene copolymers with various amounts of oil per hundred parts of polymer. (See Table XX, Reference 40, Figs. 2A and 2B.)

suggests that the high *cis* 1,4 polymer is a suitable replacement for natural rubber¹⁰⁹. As such, it would compete with the *cis* 1,4 polyisoprene polymer^{110, 111} that was developed concurrently and, indeed, was the first to have appeared in commercial quantities¹¹². Indeed, the Shell Chemical Company have just announced the availability of a 25-part oil-extended polyisoprene⁹⁵ at a price competitive with cold SBR. This commercial information makes it even more pertinent to examine the possibility of oil-extension in the case of *cis* 1,4 polybutadiene although there are insufficient references in the literature, at present, to allow more than reasonable speculation.

An excellent discussion of the various stereospecific catalysts, the possible chain structures, and the effect on the physical properties is outlined by Sittig¹¹³ for polyethylene. *Cis* 1,4 polybutadiene¹⁰⁹ is prepared in a hydrocarbon medium and the *cis* 1,4 content is reported to be higher than 95%. The polymer has a very high resilience¹⁰⁸ and the power loss⁹⁹ is maintained at a low level over a wide range of temperatures. Experimental *cis* 1,4 polybutadiene polymers have been used to prepare tire tread stocks, either alone or in blends with natural rubber, and road tests¹¹⁴ have indicated that the wear resistance is superior to that of natural rubber.

This evidence that *cis* 1,4 polybutadiene has a combination of processability and physical properties suitable for tire applications presents an opportunity to examine the role of chain structure in oil extension. A comparison of the behavior of the high *trans* 1,4 SBR copolymer, SBR, and *cis* 1,4 polybutadiene might lead to further developments in the field of oil-extended rubbers.

C. ALKYL LITHIUM-CATALYST POLYMERS

A further type of new catalyst for the polymerization of butadiene or isoprene, was announced in 1958¹¹⁵. "Diene Rubber", a polybutadiene polymerized in a hydrocarbon medium by an lithium alkyl catalyst, has been described by Smith¹¹⁶. This polymer has a mixed structure composed of *cis* and *trans* 1,4 and 1,2 units and, thus, differs from the high *cis* 1,4 polymers produced with an aluminum alkyl/metal halide catalyst. The average molecular weight is said to be high and the rubber is difficult to handle on a mill when the Mooney viscosity is over 60. It is compatible with natural rubber, however, and such blends have satisfactory processing and physical properties. Diene rubber is compatible with petroleum oils and tests are described¹¹⁶ in which up to 20 parts of an aromatic-type oil were employed in the compound. The higher loadings of oil produced a considerable decrease in the modulus value but only a moderate change in the hardness and tensile strength of the vulcanizate.

The structural composition and molecular weight of Diene rubber appears favorable for application of the oil extension principle but further information on the effect of oil on this high molecular weight rubber is required before any conclusion may be reached.

D. ACRYLONITRILE-BUTADIENE COPOLYMERS

The NBR (acrylonitrile-butadiene) copolymers¹¹⁷ are produced by an emulsion polymerization process in a manner similar to that used for SBR rubbers. The acrylonitrile units confer a degree of oil-resistance to the copolymer that varies directly as the amount of bound acrylonitrile. The range in acrylonitrile unit content in the commercial types is between 18 and 50% and the most common level is around 35%. The normal level of bound styrene for SBR

rubbers is about 24%. It will be seen that, on a molar basis, the butadiene level in the NBR polymer is about 80% of that in an SBR rubber. Since the acrylonitrile unit is polar and a higher molar fraction of this monomer unit is present in the NBR copolymer one might expect that this condition would be less favorable for oil extension than is the case with SBR.

Acrylonitrile and butadiene may be copolymerized at various temperatures and, similarly to the SBR types, "hot" and "cold" rubbers are manufactured and a range of molecular weight products are available that have a Mooney viscosity between 50 and 100. The acrylonitrile-butadiene copolymers are not completely soluble in polar solvents, such as methyl ethyl ketone¹¹⁸ and this is an additional factor that may influence the use of softeners. The "hot" types normally have the lower raw polymer solubility in methyl ethyl ketone and range from 45 to 90% while the "cold" types are said to be more linear and have a solubility of 85 to 100%.

There have been few references to an application of the oil extension principle to NBR polymers and one reason may be that it is very difficult to prepare a high Mooney viscosity polymer without appreciable branched or crosslinked structures. These would not be easily-swollen by a petroleum oil to form a plasticized, homogeneous composition that would provide optimum physical properties. It might be necessary to employ a more-costly ester plasticizer to extend such a polymer and this would detract from the economy of the process. Furthermore, the nitrile polymers are employed most often in contact with aromatic oils and fuels and these would extract and replace the ester plasticizer in the vulcanizate. Such an effect would produce even more significant changes in the vulcanizate properties of an extended rubber than for a normal NBR vulcanizate. It would present a rather difficult problem for use in contact with a number of different fluids. In order to complete the picture, coarser carbon blacks are employed to a larger extent in NBR compounds because higher loadings of these materials may be used without generating excessive temperatures during the mixing operation. The swelling resistance of the vulcanizate is improved by the presence of such large volumes of filler.

Under the circumstances described there does not seem to be much scope or economic incentive for applying oil-extension to the NBR system. It would be of interest in this review, however, to include the case of a butadiene copolymer that contains a polar monomer.

An optimum case might have a "cold" (soluble), high molecular weight NBR extended with a common type of ester plasticizer (dibutyl phthalate, for instance) to provide a lower Mooney viscosity, easy-processing product. A typical gasket-type compounding recipe was selected for this examination¹¹⁹ that contained 75 parts of SRF black and 10 parts of dibutyl phthalate (Recipe A-2¹¹⁸). The levels of this softener-filler combination were varied with a relatively high molecular weight NBR prepared in Pilot Plant equipment. The data¹¹⁸ suggest that it would be possible to match the compound Mooney viscosity and stress-strain properties obtained with a 50 Mooney viscosity NBR compound by extension of the experimental polymer with high quantities of plasticizer except for the tensile strength. The effect of a reduction in the polymer content of the compound on the tensile strength is shown in Figure 27. It is apparent that at each level of dibutyl phthalate there was a different plateau value for tensile strength. The tensile value was decreased for increasing amounts of plasticizer and this could not be balanced by a proportionate increase in the amount of carbon black. A similar effect on the tensile strength has been observed when a petroleum oil softener was employed in this study¹¹⁹.

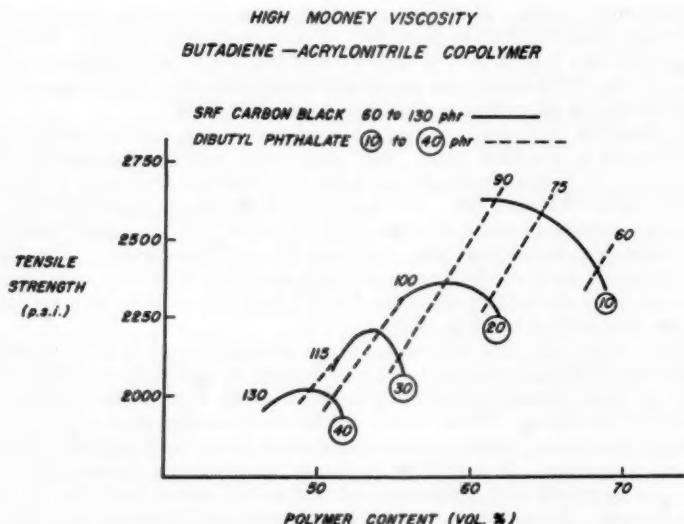


FIG. 27.—Effect of plasticizer and carbon black loading on tensile strength of butadiene/acrylonitrile copolymers (Reference 119, unpublished).

The effect of the plasticizer is better described as a dilution rather than an extension of the polymer.

Figure 13 shows the change in tensile strength observed in the SBR system by a progressive addition of softener¹¹. In this case, a definite improvement in tensile strength was obtained by the initial additions of oil and carbon black and a maximum tensile strength was provided at a polymer content of about 62% by volume. A further decrease in the polymer content by additions of either oil or carbon black produced a very similar change in the tensile strength of the vulcanizate. This figure depicts an ideal case for application of the oil-extension principle.

It appears, therefore, that the presence of a polar monomer in a butadiene chain will not be conducive to the application of the oil extension principle. It is apparent that the type of end use concerned may dictate the type of compounding ingredients to be employed and have a bearing upon the applicability of the oil extension principle.

VII. NEOPRENE

Neoprene, a homopolymer of chloroprene, was one of the first successful types of synthetic rubber². The presence of chlorine in the monomer molecule confers a significant degree of oil resistance to the polymer¹²⁰ and, like natural rubber, the vulcanized polymer possesses a high pure-gum tensile strength. The addition of reinforcing carbon blacks to the polymer will increase the tensile strength somewhat²² and the other stress-strain properties reflect the normal reinforcement effect of added fillers.

Neoprene is compatible with relatively large volumes of aromatic-type petroleum oils¹²⁰.

The general purpose types of neoprene have a Mooney viscosity about 50 and high molecular weight polymers are produced whose Mooney viscosity may be as high as 130. The inverse relationship between the tensile strength and the polymer content of the vulcanizate is a common characteristic for the polymers in this entire range of average molecular weights. It is reported¹²¹ that the average molecular weight does not produce a significant change in the physical properties of the vulcanized polymer in the Mooney viscosity range of 50 to 100 while some increase in quality is attained at still higher molecular weight levels.

These basic properties, then, suggest that the application of the oil-extension principle to neoprene would be a practical and technically-desirable method of effecting economies in the use of a raw material. The effect of increased loadings of softener and filler¹²² on the tensile strength of the vulcanizate is more similar to that of natural rubber than the SBR or NBR types and it may be desirable to adopt a somewhat modified approach.

Historically, the evolution of neoprene polymers^{121, 122} has followed a course remarkably parallel to that taken by the SBR polymers. Thus, the first commercial series of neoprene polymers, or G-types, were modified with a sulfur or thiuram stabilizer. An unmodified, highly crosslinked chloroprene polymer (Neoprene Type S) was introduced in 1947 and found a special application in crepe soling. This was a high molecular weight polymer that could be blended in minor amounts to increase the viscosity of the G-types. Further developments in the polymerization of chloroprene resulted in the production of a new series of polymers (W types) that did not require a sulfur or thiuram stabilizer. These polymers showed a higher level of tensile strength in loaded stocks, better resistance to mechanical breakdown and a better balance of processability and physical properties when high loadings of softener and fillers were present than did the previous series of neoprene polymers (G types). These improved characteristics led to the use of higher loadings of softener and filler in commercial vulcanizates and, in 1953, a higher viscosity polymer (Neoprene Type WHV) was introduced that had a Mooney viscosity in the range of 110 to 130. This product could be blended with the Type W polymer to produce any preferred level of Mooney viscosity and higher loadings of softener and filler were found to provide good processing properties with the higher Mooney viscosity polymer.

The similarity in the development of the SBR types from hot to cold polymerization systems, with a resulting improvement in physical properties, and finally to high molecular weight polymers capable of oil extension, is a striking one.

Neoprene is well recognized as an oil-resistant type of polymer¹²⁰ and some case must be used to select oils so that they will be compatible in the uncured compound and the vulcanizate. The relatively-paraffinic type oils swell neoprene vulcanizates only to a limited extent and the resistance to swelling varies inversely with the aromaticity of the oil. Thus, while loadings of the relatively-naphthenic type oils may be used up to 20 parts without exudation from the compounds, the relatively-aromatic type oils may be required when higher loadings are employed in neoprene. Generally, if there are fractions of an oil present in a neoprene compound beyond their compatibility limits, a bloom will appear on the uncured stock or the vulcanizate at some period after cure. Thus, to be compatible with neoprene at an equal weight loading, the aromatic content of the oil should be 75% or more¹²², as determined by the silica gel ab-

sorption, and straight-chain paraffins should not be present in amounts exceeding 0.5%. The amount and type of filler employed in the compound may affect the compatibility limit of an oil in neoprene through occlusion or absorption on the filler, as occurs with other types of polymer. Also, lower viscosity oils are found to be more efficient softeners although the higher viscosity oils are desirable for most processing requirements because the stock resists distortion better during handling prior to vulcanization. The relatively-aromatic type oils, of course, are darker in color and contribute staining and discoloration tendencies in light-colored compounds.

The low-cost fillers of the calcium carbonate class generally are not recommended for use in neoprene because they impair the weather and ozone resistance severely when used in large amounts¹²⁴. Clay is the preferred light-colored filler for neoprene compounds and, while high loadings result in a lower level of tensile strength than an equal volume of carbon black, economical and attractive colored vulcanizates may be obtained when employed with a balanced loading of a relatively-naphthenic type oil. The thermal carbon blacks and semireinforcing furnace types are preferred for use in neoprene to provide a good balance between processing and physical properties and economic considerations. The carbon blacks having a finer particle size and higher structure provide smoother processing and less plastic uncured compounds but do not result in as good a balance of cost and quality¹²². The finer furnace and channel types provide compounds that can tolerate a higher softener-to-filler ratio to give the same hardness and modulus level obtained with the "softer" carbon blacks. It appears that the reinforcing potential of "hard" carbon blacks is not efficiently utilized in neoprene compounds at moderate loading of black.

The examination of the extension of the neoprene polymers¹²² with oil and filler showed that, unlike SBR, chloroprene polymers of such a high viscosity as to require large amounts of oil in their compounds may be mixed and processed with ease. Little, if any, difference existed between vulcanizates made from polymers to which oil had been added during their manufacture and those which had been extended with the same oil during the mixing of the compound¹²¹.

With the earlier types of neoprene, the degree to which the Type G polymer could be extended with softener and filler was limited from the standpoint of both processability and vulcanizate quality¹²³. Thus, high loadings resulted in an extremely mushy and putty-like compound and the tensile strength and compression set properties of the vulcanizate were markedly impaired. In order to improve processability, large quantities of vulcanized vegetable oil were often used as an extender but this method is not a particularly economical one in view of the reduction in the quality of the vulcanizate when high loadings are present.

The high molecular weight polymer, Type S, was found to improve the processability of highly-plasticized neoprene compounds by its effect in raising the viscosity when blended with neoprene, Type G. The difference in the viscosity of these two polymers, however, gave rise to problems in preparing a homogeneous blend during mixing operations. The principle disadvantage to the use of Type S in blends was that the increase in viscosity was accompanied by a disproportionately great increase in elasticity, or "nerve".

The introduction of the W type polymers, with improved resistance to breakdown and a higher tolerance to softeners with improved physical properties, led to the development of a higher Mooney viscosity, processible type of Neoprene (Type WHV). Blends of this polymer and Type W could be em-

ployed to adjust the viscosity of compounds containing a low percentage of polymer so that a suitable level of processibility was obtained under normal factory conditions.

A comparison of the properties of vulcanizates prepared from neoprene polymers having a widely-different viscosity is clouded by a number of factors not directly related to molecular weight. One of these may be the ability of the chloroprene chains to associate in a higher ordered state when exposed to moderately low temperatures. This is referred to as a crystallization of the polymer and it may be noteworthy that neoprene vulcanizates containing higher loadings of softener and filler show a relatively slight stiffening after long term exposure at the optimum temperature for crystallization (approximately 32° F)¹²². It is not unexpected that, in a more highly-loaded compound, the association of polymer chains would be hindered simply because their volume concentration is lower and one might conclude that any contribution of "crystallization" to tensile strength would be less in such cases while a smaller effect

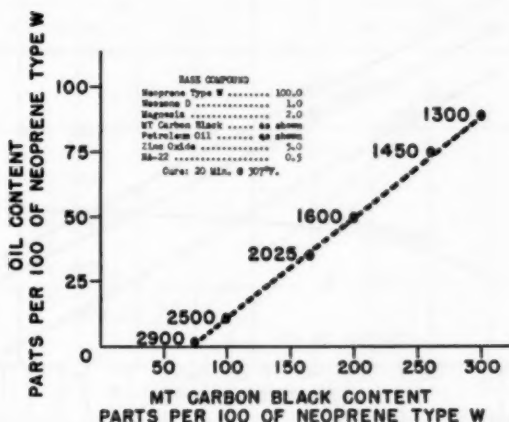


FIG. 28.—Quantities of MT carbon black and oil required for 60 durometer neoprene type W compounds of various tensile strength. (Reference 122, Fig. 1.)

would be apparent on the modulus or hardness at room temperatures. In this connection, it is stated¹²¹ that "measurable differences in such properties as tensile strength, stress relaxation and resilience exist only when the viscosity difference is greater than approximately 50 Mooney units". Thompson concluded that higher molecular weight chloroprene polymers may be extended further with filler and softener than those of lower molecular weight with an apparently disproportionately lower sacrifice in vulcanizate quality.

Neoprene Type G and Type W polymers may be crosslinked with zinc oxide. The G types are the faster curing, however, and it is customary to employ an organic accelerator (NA-22) with W types in addition to zinc oxide. The higher molecular weight polymers tend to cure a little faster than the lower Mooney viscosity products. However, the accelerator level required for equivalent cure rate in the higher molecular weight polymer is generally higher since these employ high loadings of filler which result in a retarding effect.

In summary, there are a number of striking similarities in the case for oil extension of NBR and neoprene polymers although the two polymers possess quite distinctive properties from other points of view. These two polymers are employed in mechanical goods where oil resistance is a basic consideration. The desired properties are best obtained by employing relatively high loadings of semireinforcing grades of carbon black and a moderate loading of softener is normally present to aid in processing, to adjust the hardness and stiffness of the vulcanizate to suit the end use (Figure 28), and to achieve a desirable cost-quality balance since both of these rubbers are more expensive than a general-purpose SBR. These considerations make a direct application of the oil-extension principle, as specifically defined for the case of SBR treadstocks, a less attractive approach in the case of neoprene polymers. It is undoubtedly true that these design principles could be applied to a high molecular weight

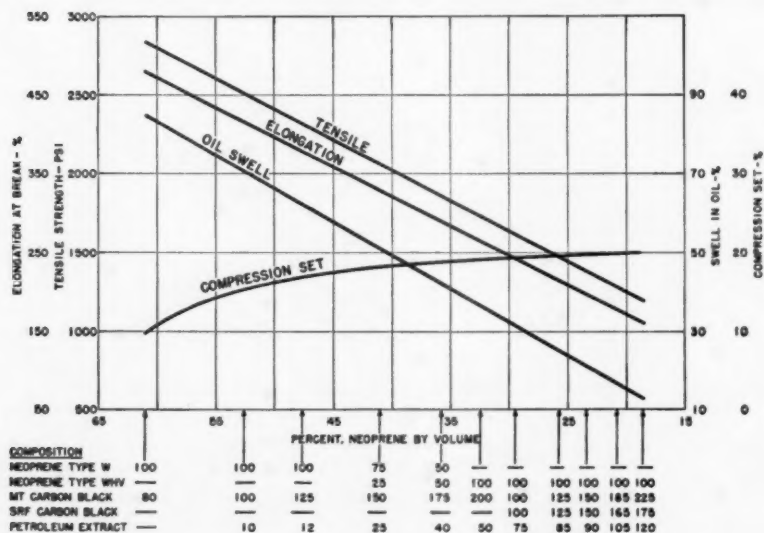


FIG. 29.—Physical properties of 60 to 70 durometer hardness compounds of varying elastomer content. (Reference 123, Fig. 1.)

(Type WHV) polymer and that suitable softener-filler loadings could be selected to provide an extended neoprene that would show all the essential processing and physical property characteristics of a lower molecular weight Type W polymer. When the principle uses of the polymer lie in the mechanical goods field however, such calculated adjustments in the masterbatch composition do not provide any real advantage in simplifying the compounding approach. Moderate extension of a high molecular weight neoprene polymer would not provide any advantage in the cost or ease of preparing the masterbatches and the product would be employed simply for further additions of these two classes of compounding ingredients to achieve the desired balance of properties.

Neoprene polymers of quite different molecular weights may be readily mixed with large amounts of softener and filler on mechanical equipment to

provide processible compounds with suitable vulcanizate properties. The scope provided by Neoprene Types W and WHV in such applications is amply illustrated in Figure 29¹²³.

VIII. BUTYL RUBBERS

Butyl rubbers are copolymers of isobutylene and isoprene¹²⁵ in which the unsaturation provided by the addition of isoprene monomer is kept at a low level.

The monomers are polymerized at a very low temperature (-140°F) in a halogenated hydrocarbon media by an ionic mechanism that employs aluminum chloride as the catalyst. Commercial polymers are available with a molar unsaturation in the range of 0.5 to 3.0%. This level of unsaturation is sufficient to provide a satisfactory crosslink density during sulfur vulcanization although the polymer is slower-curing than SBR rubber and requires a relatively high level of ultra accelerators. The low degree of unsaturation, however, is essential to provide the unique characteristics possessed by this copolymer, namely, excellent aging and resistance to ozone-cracking combined with a very low permeability to air and many other gases.

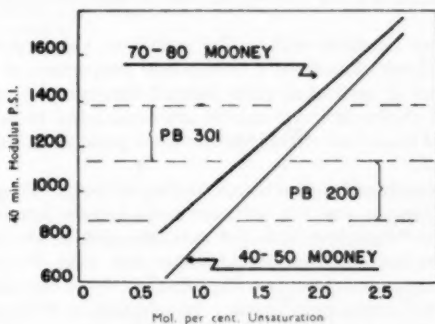


Fig. 30.—Effect of molecular weight and unsaturation on the modulus of butyl rubber vulcanizates. (Reference 127, Fig. 2.)

The ability to retain air and to resist high temperatures¹²⁷ made butyl rubber an ideal polymer for use in inner tubes¹²⁶ and, originally, the entire volume of production of this polymer was devoted to this one application. Indeed, the compounding knowledge required to use butyl rubber was confined at first to a single recipe with very minor variations in any of the several basic compounding ingredients. This stage has long-since passed and the properties of butyl rubber have made it a desirable polymer for use in many different applications that require excellent aging and chemical resistance. While there has been a large increase in the diversification of its applications in the past ten years, the majority of the uses are in the mechanical goods field, and two of these represent a very significant proportion of the total volume consumption. These are in inner tubes and in the curing bags and bladders employed in tire-curing molds and Bag-O-Matic presses, respectively. The typical recipes for these two types of product employ SRF, HMF and FEF carbon blacks at a total loading of 50 parts per 100 parts of butyl rubber and about 5 parts of

softener is normally present as a processing aid. The existence of a large-volume end use that involves a medium level of carbon black and a minimum loading of softener presents a nearly-ideal condition for application of the oil-extension principle.

Butyl rubbers¹³ are produced to have various average molecular weights that correspond to mean Mooney viscosity (ML/8', 212° F) values of 45, 55, 65 and 75. The original type of polymer was standardized at the lower Mooney viscosity value and had an average molecular weight of about 325,000. The highest Mooney viscosity level corresponds to an average molecular weight of 500,000 and, while somewhat higher molecular weight products may be obtained in this system, the Mooney machine can not provide a measure of their viscosity because the polymer shears and unreliable results are obtained for values above 80⁴⁵. The 45-Mooney polymers are produced at five levels of unsaturation ranging from 0.8 to 3.0 mole-per cent while the higher molecular weight polymers of interest in this study have a common unsaturation level of 1.8 mole-%. In the butyl rubber system there is a marked effect of unsaturation and molecular weight on the modulus of the vulcanized polymer¹²⁶ (Figure 30) and an increase in either factor provides a higher modulus; the unsaturation level has the more-pronounced effect and, hence, the effect is usually referred to as a "faster cure rate". This situation is a very beneficial one for application of oil extension as will be seen later.

The crosslinking reaction with sulfur occurs at the isoprene units in the polymer chain. These units form a very minor proportion of the chain which is largely composed of saturated units formed through the polymerization of isobutylene. The chains in butyl rubber are considered to be linear although minor quantities of branched chains appear to be possible in the higher molecular weight polymer.

The softeners employed in the compounding of butyl rubber are relatively-paraffinic oils and waxes and the softener must have a low iodine number in order that it will not interfere with the vulcanization of the low-unsaturation polymer¹²⁶. While the relatively-naphthenic oils may be used with butyl rubbers, they are more compatible with paraffinic-type oils and these are preferred because of the lower pour point. In addition to their softening action, the plasticizer employed in butyl compounds should provide some degree of flexibility at low temperature and, indeed ester-type plasticizers¹²⁶ are often used to provide a significant improvement in these properties.

The low temperature problem of butyl vulcanizates involves several factors and was the basis of an intensive study to improve the performance of early types of inner tubes which showed a pronounced tendency to growth under winter temperature conditions¹²⁶. The deformation of the inner tube from contact with the road did not recover in the period before a succeeding contact and, as a result the tube grew in diameter and eventually folded back on itself at a location near the crown of the tire. This fold caused chaffing of the tube during the travel of the car which finally produced a pin-hole allowing the tube to deflate and the tire became unserviceable until the tube could be replaced, or repaired.

This behavior was primarily a result of the low retraction rate of the butyl vulcanizate at ambient temperatures. Butyl rubber vulcanizates are remarkable for their low resiliency at room temperature which is stated to result from a high internal viscosity¹²⁷ occurring through the mass of methyl side groups attached to the polymer backbone chain of isobutylene units. The internal viscosity rises rapidly with decreasing temperature according to Fox and

Flory¹²⁸ and a leathery state is reached around a temperature of 0° F. In order to increase the rate of retraction at these temperatures it is necessary to either reduce the internal viscosity of the vulcanizate or to increase the elasticity of the network through the introduction of additional crosslinkages.

The effect of addition of plasticizer is to shift the minimum in the resilience-temperature curve to lower temperatures (Figure 31) i.e., reduce the internal viscosity. As the viscosity of the plasticizer becomes lower, the resilience and retraction rate of the butyl vulcanizate both increase. It was believed¹²⁹ that a paraffinic or naphthenic oil with a viscosity in the region of 75 centipoises at 80° F would provide the best balance of physical properties. It is of interest to note that, if the plasticizer viscosity is plotted against the rebound of the vulcanizate (Figure 32), the points for both ester and for hydrocarbon oils apparently lie on the same curve.

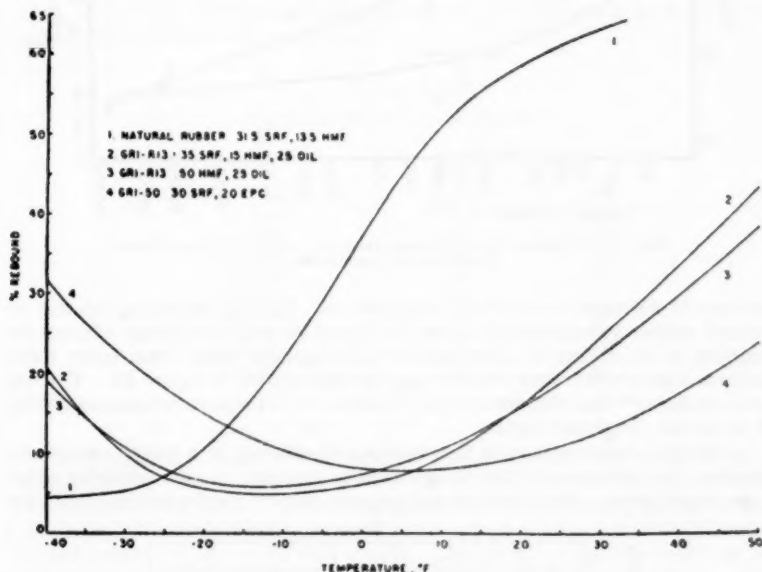


FIG. 31.—Temperature-rebound relationship of various butyl rubber inner tube stocks. (Reference 126, Fig. 5.)

Figure 32 also shows the effect of viscosity on the oil loss of plasticizer from the vulcanizate through migration or diffusion at normal temperatures. The loss of plasticizer¹²⁸ from the butyl inner tube by migration into the tire carcass would cancel any beneficial effects upon the performance at low temperatures. The results of laboratory and service tests indicated that an oil with a viscosity of about 75 centipoises at 80° F would migrate to an extent of 16 to 20% during a summer of average driving and this provides a measure of the minimum viscosity that will provide a satisfactory service performance under such conditions.

The low permeability to air is a major factor in the use of butyl rubber in inner tube service and this property is influenced to a significant degree by the

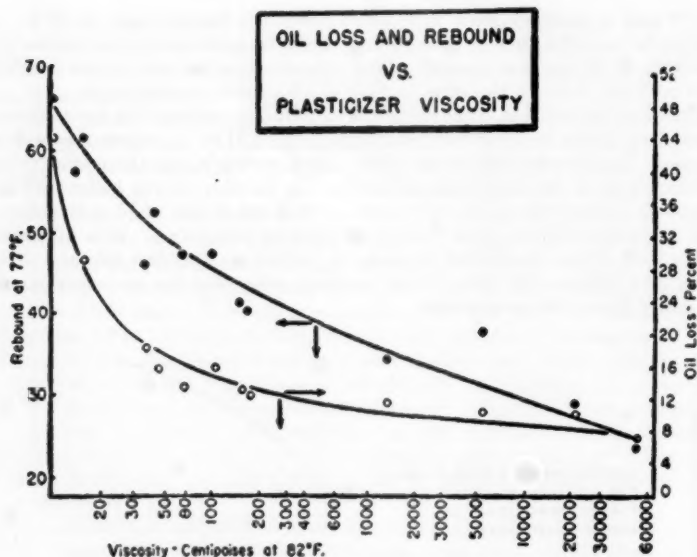


FIG. 32.—Oil loss and rebound versus plasticizer viscosity for butyl rubbers (Reference 129, unpublished).

amount of softener in the butyl vulcanizate. The air retention relative to natural rubber vulcanizates is given in Figure 33 and the change effected by addition of plasticizer is quite marked although air losses from inner tubes indicate a somewhat lower effect in service than shown in Figure 33. There is some evidence¹²⁷ that the permeability is increased in proportion to the solubility of air in the plasticizer itself.

A further disadvantage to the presence of softener in a butyl vulcanizate involves the resistance of the vulcanizate to cracking in air containing small amounts of ozone. Butyl rubber vulcanizates show a greater tendency to form

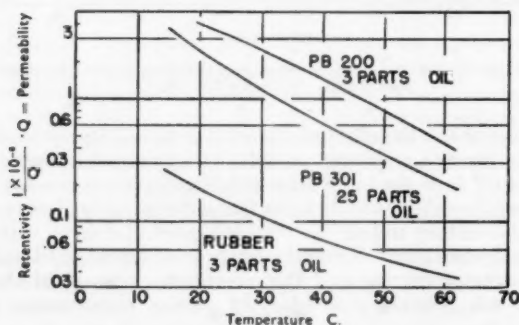


FIG. 33.—Effect of molecular weight and oil loading on the permeability to air of butyl rubber inner tube vulcanizates. (Reference 127, Fig. 5.)

ozone cracks for polymers containing a higher degree of unsaturation¹²⁰ or at high loadings of plasticizer. The resistance to ozone cracking is a valuable characteristic of butyl vulcanizates and many applications in the mechanical goods field are based upon its superior resistance to ozone. The addition of softeners, therefore, must be made with caution if this property is a factor in the performance of the article in service. Edwards¹²⁰ has suggested that this tendency occurs through a dilution of the network concentration by the presence of the softener and that it may be counteracted by providing an increase in the crosslink density of the vulcanizate.

The application of the oil-extension principle to butyl vulcanizates requires the consideration of a number of novel physical and chemical factors that are peculiar to butyl rubbers. Most of the effects resulting from the presence of a softener are beneficial while others may not be desirable in all applications. This prior experience in the use of softeners in butyl rubber inner tubes indicates that, at least in this high-volume application, the balance is in favor of the use of moderate loadings of softener.

TABLE XXI
OIL CAPACITY OF BUTYL POLYMER*

Molecular weight	Oil capacity (phr)	
	Mooney viscosity	Cold flow
280,000	14	13
439,000	25	25
650,000	36	37
800,000	28	40
900,000	35	46
980,000	38	43
1,115,000	30	48
1,250,000	43	48
1,400,000	36	50

* Reference¹²⁹.

The basic advantage of a softener is that it increases the plasticity of the rubber so that the processability will be improved during the mixing and shaping operations. The effect of a relatively-paraffinic oil in softening the linear butyl polymer is relatively large compared to the effect produced in an SBR rubber of the same average molecular weight. The effect of various loadings of a relatively-paraffinic oil (Polar 45) on the compound Mooney viscosity and the cold flow property are shown in Table XXI. The cold flow test is essentially similar to a Williams plasticity test and it is used to measure the resistance of the shaped compound to distortion before vulcanization. The amount of softener required to adjust the compound Mooney viscosity, or the cold flow property, to a suitable performance level varies directly with the average molecular weight of the butyl rubber. This value, indicated here as the oil capacity, is comparable to the term "oil demand" that was employed in the discussion of SBR rubbers. The actual softener loadings mentioned, however, were not estimated on a comparable basis by these two independent investigators and do not correspond in the two cases. It is interesting to note that these two estimates of the oil capacity of butyl rubber indicate similar trends with an increase in either the softener loading or molecular weight and, in both cases, the cold flow characteristic is a less-limiting factor than the loading required

to produce an equal value for the compound Mooney viscosity. These data allow an estimate of the oil capacity of a 75-Mooney compared to a 45-Mooney Butyl rubber. When the average molecular weights are taken as 500,000 and 325,000, respectively, the oil capacity are estimated to be 29 and 17 phr in an inner tube recipe. The increase in oil capacity decreases markedly at higher average molecular weight levels in the manner predicted on theoretical grounds²⁸ and this supports the hypothesis that at infinite molecular weight only a slight increase in oil demand may be expected if quality is to be considered as the basic criterion.

It is known from the work of Mullins¹³¹ that all pigments adversely affect the internal viscosity and resilience of the vulcanized rubber and, hence, the amount used must be kept to a minimum as determined by processability and service requirements. Since butyl rubber is a linear polymer having a very regular spacing of methyl side-groups, it can form an ordered alignment of chains on stretching and is known to crystallize at high strains. Thus, the tensile strength is a maximum at a pigment loading near zero and this property varies directly with the volume of polymer in the vulcanizate.

It has been demonstrated in laboratory work¹²⁶ that the finer the particle size of the carbon black the greater is the effect of this pigment to increase the internal viscosity. This conclusion favors the use of SRF and HMF types of black rather than channel blacks. Indeed, at the customary 50-part loading, inner tubes were found to be less subject to "cold-buckling" when a high ratio of SRF to HMF black was employed as would be predicted from the smaller particle size of the HMF carbon black.

Further consideration of the mechanical processes involved in the formation of buckles in inner tube suggested that an improved resistance could be expected from an increase in the modulus of the vulcanizate at a given level of internal viscosity. A higher state-of-cure would be desirable and this was achieved by employing a higher unsaturation level and average molecular weight in the butyl rubber¹²⁶ and vulcanizing the compound at a higher curing temperature. The temperature range adopted in North American practice was from 330° to 350° F, and desirable rates of production were achieved at this level. Butyl rubbers with a still higher average molecular weight¹²⁷ were developed to provide a more-elastic network and small amounts of difunctional organic compounds¹³² were employed in a so-called "heat treatment" of the rubber, or rubber-pigment masterbatch, during the mixing operation. This procedure employs para dinitroso benzene, para quinone dioxime, or N,P-dinitroso-N-methyl aniline, in quantities less than 0.5 parts to achieve a small degree of chemical crosslinking of polymer-to-polymer, or polymer-to-carbon black by subjecting the polymer and chemical to temperatures over 320° F for a short time during the mixing cycle. This precure crosslinking of the polymer needed careful control for processing reasons¹³³. Its use infers that a higher softener loading could be employed to take advantage of the two means of reducing the internal viscosity, i.e., higher levels of crosslink density and softener content.

It will be apparent at this stage in the discussion that the "cold-buckling" problem in butyl rubber inner tubes was resolved by an oil-extension principle and, indeed, this was the first commercial application of the procedure that was adopted in the SBR field some five to six years later. In the case of butyl rubber, however, the high molecular weight polymer was a processable type and the oil loadings involved were moderate ones so that it was possible to produce the desired level of extension during the compounding operation. The "heat-treatment" of the butyl rubber provided a chemical means for the rubber

manufacturer to adjust the softener-processability level of the polymer to suit his factory operations and select the most appropriate softener, or combination of softeners, to achieve the desired properties in the vulcanizate. Under such conditions, it was more advantageous for the rubber manufacturer to add the softener to the polymer during the compounding procedure than to have a masterbatch prepared in the synthetic rubber plant. One further economic factor that may be mentioned at this point involves the high degree of cold flow of the early butyl rubber which required special attention in packaging the raw rubber. The masterbatching of liquid softeners with the butyl rubber would have increased this tendency and presented a very difficult problem. One rubber producer, in fact, devised an unique shipping package in order to facilitate export shipments of butyl rubber; a sealed metal can.

In retrospect, it is of interest to observe how the rubber manufacturer modified the butyl rubber inner tube recipe and the similarity between this approach and the method outlined for the oil-extended SBR rubber. The carbon black and softener loadings that are employed for butyl rubber inner tube compounds at each of the two levels of Mooney viscosity are shown in Table XXII. We may regard this amount of oil to consist of the normal load-

TABLE XXII
OIL-EXTENSION OF BUTYL RUBBER INNER TUBE RECIPE*

Butyl rubber (45-Mooney: 1.4 mole %)	100	—
Butyl rubber (75-Mooney: 1.6 mole %)	—	100
FEF carbon black	20	25
SRF carbon black	30	35
Paraffinic-type oil	5	25
Zinc oxide	5	5
Stearic acid	0.5	0.5
Mercaptobenzothiazole	0.5	0.5
Tetramethylthiuram disulfide	1.0	1.0
Sulfur	2.0	2.0
Modulus at 400%, psi	770	695
Tensile strength, psi	2310	1975
Elongation at break, %	735	700

* Unpublished data.

ing of 5 parts that serves as a process aid and a further 20 parts added as extender to compensate for the higher molecular weight of the polymer. Adopting the nomenclature applied to SBR masterbatches, it is clear that the combined carbon black loading is held constant at 50% of the weight of rubber plus extender oil. By coincidence, the butyl rubber inner tube and the oil extended rubber tread recipes both employ a 50% carbon black loading as the standard level.

A comparison of typical stress-strain properties are shown in Table XXII for these two recipes. The balance of molecular weight and softener is sufficient to achieve identical vulcanizate characteristics but the versatility of the butyl rubber system provides a means of adjusting the modulus level by small changes in the unsaturation level of the polymer (monomer ratio) or by the formation of crosslinked structures in the polymer during the mixing operation (Polyac, Elastopar, etc.). The tensile strength of the vulcanizate is relatively unaffected by the physical and chemical changes resulting from a combination of the factors affecting average molecular weight, crosslink formation and softener addition provided that a suitable state-of-cure is attained during vulcanization. It is

unfortunate that the universal tendency in the butyl rubber field is to relate the initial modulus to the state-of-cure. More-proper estimates of state-of-cure are those generally accepted by rubber technologists as a measure of the cross-link density in the vulcanized polymer network, i.e., relaxed modulus, relaxed compression set, swelling resistance, etc.

The compounding and vulcanize characteristics of butyl rubber need not be discussed at greater length in this review. References to such data are many and in considerable detail^{127, 133, 134}. It may suffice to indicate that the higher molecular weight polymer has largely replaced the original 50-Mooney polymer in all applications of butyl rubber, except those few cases where the presence of a mineral oil may not be permitted in intimate contact with certain drugs, etc. It is a general practice to employ 20 to 35 parts of softener in butyl rubber compounds and this is viewed by compounders as a normal characteristic of the rubber.

One can not help but compare this viewpoint to the continuing controversy in the oil-extended rubber field of SBR polymers concerning the role of softener and the proper basis for selecting filler and curative levels. Albeit the SBR field of end use is a much more complex one than even that of butyl rubber. The situation is rapidly changing, however, and more and more applications in the mechanical rubber field are employing butyl rubber in addition to the large-volume uses in inner tubes and curing bladders. One need only cite the commercial introduction of 100% butyl rubber tires to indicate the increasing range of application for this rubber¹³⁵.

IX. ETHYLENE-PROPYLENE RUBBERS

A new class of copolymers has received considerable attention in the synthetic rubber field during the last few years although no commercial products have appeared on the market. These are the EPR (ethylene-propylene rubbers)¹³⁶ produced by the application of Ziegler-Natta catalysts in a hydrocarbon media. A further member of the stereoregular group, these copolymers may be saturated or unsaturated and those containing between 40 and 60 mole per cent of propylene units have interesting rubbery characteristics. Polymers with higher proportions of ethylene are said to be of value in thermoplastic applications. While little is known at this stage concerning their potential in the rubber field, some information in current literature^{137, 138}, may be useful to form a preliminary estimate.

The saturated polymers require specific agents to crosslink the propylene units in the polymer chain. Peroxides are mentioned as vulcanizing agents¹³⁹ but only dicumyl peroxide and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane are known to produce vulcanization of this polymer. Aromatic-type oils may not be used in such compounds since they contain fused benzene rings which consume free radicals and retard the cure. The unsaturated polymers may be cured with sulfur in a butyl-type recipe.

It is reported that these copolymers may be produced in a range of molecular weight levels and that the plasticity may be varied by changing the monomer ratio as well as the molecular weight of the copolymer. The ethylene-propylene rubbers have a high pure-gum tensile strength that is reduced by the addition of carbon black to a value in the range of 2000 to 3000 psi. The addition of carbon black stiffens the polymer to a degree that, for an addition of 50 parts of HAF carbon black, a raw polymer Mooney viscosity of 30 to 40 would be

needed to provide the same compounded Mooney viscosity as that given by an SBR type.

The EPR types are more resistant to aromatic liquids than SBR products but show less resistance to aliphatic liquids. Thus, blends of EPR and paraffinic-type oils have a lower viscosity than blends with aromatic-type oils. The addition of paraffinic or naphthenic-type oils to EPR compounds is reported to reduce the modulus of the vulcanizate. This effect is not thought to be a serious one although only ten parts of oil were added to the compound.

Certain experimental EPR types have been employed to construct tire treads¹⁴⁰ and the wear resistance was said to be suitable for passenger car service. Gelinas⁹⁸ has estimated the wear rates of a 50-part HAF compound to be similar

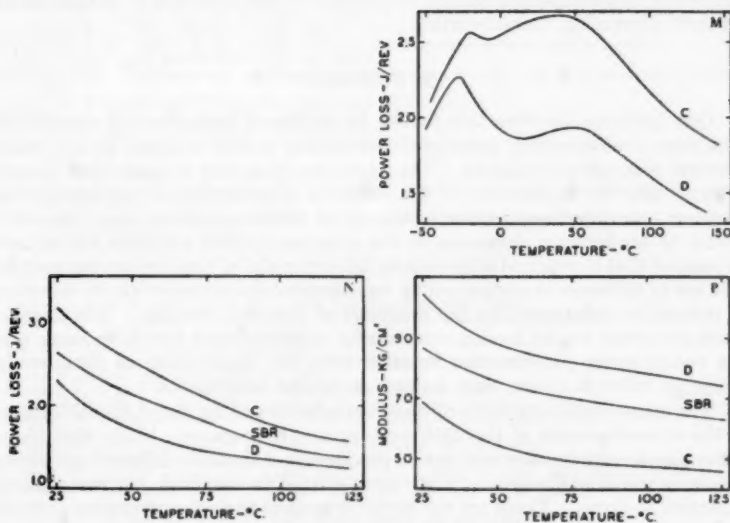


Fig. 34.—Variations of modulus and power loss of ethylene/propylene copolymers with temperature. (Reference 138, Fig. 4.)

- C 60/40 mole % copolymer with 37.5 parts of oil.
- D 50/50 mole % copolymer.
- M Power loss/cycle under 20-kg load.
- N Power loss/cycle under 10% strain.
- P Dynamic Modulus.

to those of a cold SBR vulcanizate over a range in severity conditions. The stress-strain properties were similar to those obtained with an oil-extended rubber tread compound and it was reported that the experimental EPR compound had a Mooney viscosity of 80. The power loss-temperature relationships reported by Briggs⁹⁹ and by Dingle¹³⁸ show that an EPR tread vulcanizate has a lower power loss than a cold SBR vulcanizate. When an EPR was extended with 37.5 parts of oil¹³⁸ (Figure 34) a considerable reduction occurred in the dynamic modulus of the vulcanizate. The power loss was increased to a value higher than that obtained for a cold SBR tread vulcanizate and to a degree similar to that reported for an oil-extended SBR product⁹⁹.

Since the saturated copolymers require special vulcanizing agents, one might conclude that they would provide excellent resistance to ozone and chemical agents and see extensive service as specialty rubbers in the mechanical goods field. Indeed, the present information suggests similarities between ethylene-propylene copolymers and the butyl rubbers and the early comments have suggested applications which would compete with general-purpose SBR rubbers, presumably because the monomers are relatively cheap and available in large volume from the petroleum industry.

It would be premature to engage in further speculation at this early date on the possibility of applying the oil-extension principle to the new ethylene-propylene copolymers. The announced properties of these copolymers appear suitable in many respects but further information is needed on the viscoelastic properties of these polymers and, in particular, the influence of petroleum oils on their processing characteristics.

X. SUMMARY

One hesitates to close this review by adding a paragraph of conclusions. The term "oil-extension principle" introduced a new concept to the manufacturer of synthetic rubbers. The principle (if it may be identified by such a word) and the application of the products it generated do not involve any novel or unfamiliar approaches to the art of rubber compounding. Indeed, it would be rendering a disservice to the progress of their adoption by industry to suggest that it required a revision in the viewpoint of the rubber compounder. The use of softeners in compounding was almost coincidental with the discovery of rubberlike substances by the explorers of the 16th century. The development of carbon blacks having more useful characteristics in rubber came after the compounder had become familiar with the application of innumerable inorganic fillers in rubber and, indeed, soots and lampblacks.

The tailor-made synthetic rubbers were developed by the chemical industry in the second-quarter of the 20th century and it is scarcely likely that higher molecular weight types would not be produced nor that any inherent processing problems would not be solved when there existed an economic and raw material incentive to do so. These are the contributions of the polymerization chemists and the synthetic rubber industry. Where it is more economically-attractive and technically-desirable to add softener and filler to the synthetic rubber in the manufacturing process, oil-extended rubbers and filler masterbatches will be provided as raw materials for the rubber industry. If on the other hand, these ingredients may be added quite readily during factory mixing operations, without any detrimental effects on the polymer quality, the synthetic rubber producer would be quite unwise to attempt to usurp the functions of the rubber manufacturer.

The income of the rubber manufacturer, depends upon the skill and economy that he applies to the operation of mixing rubber with liquid and solid materials and this is the prime occupation of a rubber compounder. It would avail the synthetic rubber producer nothing to try and convince the compounder that he is doing something novel and unusual by preparing softener-filler masterbatches. However, the compounder will be receptive to a pre-blended product that enables him to produce rubber mixes of better or different quality at an equal, or lower, cost. This is the aim and accomplishment of oil-extended rubbers.

REFERENCES

- ¹ Whitby, G. S. and Katz, M., *Ind. Eng. Chem.* **25**, 1204, 1338 (1933).
- ² Carothers, W. H., Williams, I., Collins, A. M. and Kirby, J. E., *J. Am. Chem. Soc.* **53**, 4203 (1931).
- ³ Kixmiller, R. W. and Weidlein, E. R., Jr., O. T. S. PB-13340, April 21, 1945.
- ⁴ Braendle, H. A. and Wiegand, W. B., *J. Appl. Physics* **15**, 304 (1944).
- ⁵ Rostler, F. and Mehner, V., *India Rubber World* **104**, 47 (1941).
- ⁶ Rostler, F. and Mehner, V., U. S. 2,217,918 (1940).
- ⁷ Rostler, F. and Mehner, V., U. S. 2,217,919 (1940).
- ⁸ Pollak, J., *Ind. Eng. Chem., News Ed.* **13**, 371 (1935).
- ⁹ Rostler, F. S., *Rubber Age* **69**, 559 (1951).
- ¹⁰ Brown, R. W., Bawn, C. V., Hansen, E. B. and Howland, L. H., *Ind. Eng. Chem.* **46**, 1073 (1954).
- ¹¹ Harrington, H. D., Weinstock, K. V., Legge, N. R. and Storey, E. B., *India Rubber World* **124**, 435, 571 (1951).
- ¹² D'Ianni, J. D., Hooley, J. J. and Greer, P. S., *Rubber Age* **69**, 317 (1951).
- ¹³ ASTM Designation: D1418-58T, ASTM Standards on Rubber Products, 19th Edition (1960).
- ¹⁴ Neal, A. M., *India Rubber World* **104**, 39 (1941).
- ¹⁵ Murphy, E. A., et al., *Brit.* 327,451 (May 28, 1930).
- ¹⁶ Goodyear Tire and Rubber Co., *Brit.* 391,765 (July 30, 1931).
- ¹⁷ Endres, H. A., U. S. 1,958,746 (August 28, 1934).
- ¹⁸ Marchionna, F., "Latex and Rubber Derivatives and Their Industrial Applications", Volumes I, II and III, *Rubber Age* (N. Y.) 1933 and 1937.
- ¹⁹ Wiegand, W. B., *Brit.* 250,279 (July 29, 1925).
- ²⁰ Howland, L. H., Peaker, C. R. and Holmberg, A. W., *India Rubber World* **109**, 579 (1944).
- ²¹ Geiger, L. M., *India Rubber World* **111**, 312 (1944).
- ²² Catton, N. L., "The Neoprenes", Rubber Chemicals Division E. I. du Pont de Nemours and Co. (Inc.), 1953.
- ²³ Kemp, A. R. and Stratiff, W. G., *Ind. Eng. Chem.* **36**, 707 (1944).
- ²⁴ Wood, L. A., *RUBBER CHEM. & TECHNOL.* **13**, 861 (1940).
- ²⁵ Merrick, L., *India Rubber Journal* **104**, 321 (1943).
- ²⁶ Ludwig, L. E., Sarbach, D. V., Garvey, B. S., Jr. and Juve, A. E., *India Rubber World* **111**, 55, 180 (1944).
- ²⁷ Ludwig, L. E., Sarbach, D. V., Garvey, B. S., Jr. and Juve, A. E., *India Rubber World* **112**, 731 (1945).
- ²⁸ Anon. Manufacturers Memorandum No. M. 10, U. K., Ministry of Supply, Admiralty, Ministry of Aircraft Production, (1944).
- ²⁹ Anon. Manufacturer's Memorandum No. M. 12, U. K., Ministry of Supply, Admiralty, Ministry of Aircraft Production, (1944).
- ³⁰ Stangor, E. L. and Radcliff, R. R., *Ind. Eng. Chem.* **41**, 1603 (1949).
- ³¹ Rostler, F. S. and Du Pont, H. L., *Ind. Eng. Chem.* **39**, 1311 (1947).
- ³² Rostler, F. S. and Rostler, K. S., *Ind. Eng. Chem.* **40**, 2222 (1948).
- ³³ Meyer, A. W., *Ind. Eng. Chem.* **41**, 1570 (1949).
- ³⁴ Dannenberg, E. M. and Collyer, H. J., *Ind. Eng. Chem.* **41**, 1607 (1949).
- ³⁵ Mitchell, J. M., Spolaky, R. and Williams, H. L., *Ind. Eng. Chem.* **41**, 1592 (1949).
- ³⁶ Yanko, J. A., *J. Polymer Sci.* **3**, 576 (1948).
- ³⁷ Mark, H., *Ind. Eng. Chem.* **43**, 1343 (1942).
- ³⁸ Einhorn, S. C. and McLeod, L. A., *Trans. Inst. Rubber Ind.* **29**, 281 (1953).
- ³⁹ Flory, P. J., *Ind. Eng. Chem.* **38**, 417 (1946).
- ⁴⁰ Stewart, R. A. and Williams, H. L., *Ind. Eng. Chem.* **45**, 173 (1953).
- ⁴¹ Stewart, G. H., Pfau, E. S. and Weinstock, K. V., *India Rubber World* **124**, 309 (1951).
- ⁴² Buckler, E. J. and Mitchell, J. M., Fifth World Petroleum Conference, Section IV, Paper 27, 1950 p. 275.
- ⁴³ Henderson, D. A. and Legge, N. R., *Can. J. of Research B*, **27**, 666 (1949).
- ⁴⁴ MacFarlane, R. B. and McLeod, L. A., *Third Rubber Technol. Conf.*, London (1954) p. 214.
- ⁴⁵ ASTM Designation: D-1646-59T, ASTM Standards on Rubber Products, 19th Edition (1960).
- ⁴⁶ Linnig, F. J. and Stewart, J. E., *J. Research Natl. Bur. Standards* **59**, 27 (1957).
- ⁴⁷ Rostler, F. S. and White, R. M., *Rubber Age* **70**, 735 (1952).
- ⁴⁸ Kurts, S. S., Jr. and Martin, C. C., *India Rubber World* **126**, 495 (1952).
- ⁴⁹ Kurts, S. S., Jr., King, R. W. and Sweely, J. S., *Ind. Eng. Chem.* **48**, 2232 (1956).
- ⁵⁰ Henderson, D. A. and McLeod, L. A., *Trans. Inst. Rubber Ind.* **30**, 115 (1954).
- ⁵¹ Breitman, L., *J. App. Physics* **26**, 1092 (1955).
- ⁵² Taft, W. K., Duke, J., Snyder, A. D., Feldon, M. and Landrie, R. W., *Ind. Eng. Chem.* **45**, 1043 (1953).
- ⁵³ Taft, W. K., Duke, J., Larchar, J. B., Kitzmiller, W. G. and Feldon, M., *Ind. Eng. Chem.* **48**, 1220 (1956).
- ⁵⁴ Taft, W. K., Snyder, A. D., Duke, J. T. and Mooney, H. R., *Ind. Eng. Chem.* **48**, 336 (1956).
- ⁵⁵ Taft, W. K., Duke, J. and Prem, D., *Ind. Eng. Chem.* **49**, 1293 (1957).
- ⁵⁶ Mitchell, J. M., Embree, W. H. and MacFarlane, R. B., *Ind. Eng. Chem.* **48**, 345 (1956).
- ⁵⁷ Reynolds, R. J., *Ind. Eng. Chem.* **50**, 785 (1958).
- ⁵⁸ Taft, W. K., Duke, J., Landrie, R. W., Snyder, A. D., Prem, D. C. and Mooney, H., *Ind. Eng. Chem.* **46**, 396 (1954).
- ⁵⁹ Taft, W. K., Feldon, M., Duke, J., Landrie, R. W. and Prem, D. C., *Ind. Eng. Chem.* **47**, 1077 (1955).
- ⁶⁰ Taft, W. K., Labbe, B. G. and Landrie, R. W., *Ind. Eng. Chem.* **47**, 2401 (1955).
- ⁶¹ Gale, E. E., Harris, I. W. E. and Kilbank, S. C., *Trans. Inst. Rubber Ind.* **33**, T-33 (1957).
- ⁶² Weinstock, K. V., Storey, E. B. and Sweely, J. S., *Ind. Eng. Chem.* **45**, 1035 (1953).
- ⁶³ Tramutt, H. M., Anderson, E. G., Rostler, T. S. and White, R. M., *Ind. Eng. Chem.* **49**, 1283 (1957).
- ⁶⁴ Sweely, J. S., Ferris, S. W., Peterkin, M. E. and Kurts, S. S., Jr., *Rev. gén. caoutchouc* **34**, 137 (1957).
- ⁶⁵ Ziegler, J. B., Sweely, J. S., Oberdorfer, P. E., King, R. W. and Kurts, S. S., Jr., *Proc., Internat. Rubber Conf.*, Washington (1959) p. 432.
- ⁶⁶ Dunkel, W. L., Ford, F. P. and McAteer, J. H., *Ind. Eng. Chem.* **46**, 578 (1954).
- ⁶⁷ Prem, D. C., Larchar, J. B., Trommer, N. S. and Clibourn, R. M., *Rubber World* **135**, 714 (1957).
- ⁶⁸ Howland, L. H., Reynolds, J. A. and Provost, R. L., *Ind. Eng. Chem.* **45**, 1053 (1953).
- ⁶⁹ Storey, E. B., Private Communication to Polymer Corporation Limited (1953).
- ⁷⁰ Heilm, A. F., *Ind. Eng. Chem.* **46**, 1730 (1954).
- ⁷¹ McCann, R. F., *India Rubber World* **131**, 361 (1954).
- ⁷² Rooney, H. E., Private Communication to Polymer Corporation Limited (1960).
- ⁷³ McMillan, F. M., Winkler, D. E. and Anderson, M. D., *Rubber Age* **66**, 663 (1950).

- ⁷⁴ Drogia, I., *Proc., Intern. Rubber Conf.*, Washington (1959), p. 476.
- ⁷⁵ Sperberg, L. R., Bliss, L. A. and Svetlik, J. F., *Ind. Eng. Chem.* **39**, 511 (1947).
- ⁷⁶ Sweitzer, C. W. and Goodrich, W. C., *Rubber Age* **55**, 469 (1944).
- ⁷⁷ Weinstock, K. V., Baker, L. M. and Jones, D. H., *Rubber Age* **70**, 333 (1951).
- ⁷⁸ Ericson, H. L. and Carver, L. D., *Ind. Eng. Chem.* **45**, 792 (1953).
- ⁷⁹ *Rubber Age* **72**, 89 (1952).
- ⁸⁰ Beach, K. C., Comper, L. F. and Lowery, V. E., *Rubber Age* **85**, 253 (1959).
- ⁸¹ Provost, R. L., Borg, E. L., Paige, J. L., White, W. W. and Howland, L. H., *Ind. Eng. Chem.* **48**, 455 (1956).
- ⁸² Roetler, F. S. and White, R. M., *Ind. Eng. Chem.* **47**, 1069 (1955).
- ⁸³ Sweitzer, C. W., *Rubber Age* **89**, 269 (1961).
- ⁸⁴ Dannenberg, E. M., Hagopian, E., Hall, J. P., Jr. and Medalia, A. I., *Trans. Inst. Rubber Ind.* **37**, 1 (1961).
- ⁸⁵ Braendle, H. A., Heller, G. L. and White, J. W., *Rubber Age* **84**, 431 (1958).
- ⁸⁶ Forrester, R. A., *Rubber Age* **86**, 646 (1960).
- ⁸⁷ Samuels, M. E., *Rubber Age* **86**, 649 (1960).
- ⁸⁸ Prikonskaya, N. V., *RUBBER CHEM. & TECHNOL.* **31**, 907 (1958).
- ⁸⁹ Anon, *Rubber World*, **143**, 82 (1961).
- ⁹⁰ Anon, *Rubber World* **140**, 660 (1959).
- ⁹¹ McLellan, D. E., Nettleton, J. S. and Toms, E. H., Communication by Polymer Corporation Limited to the R.R.C. Polymer Development Committee, Meeting No. 29 (Jan. 1953).
- ⁹² ASTM Designation D-1416-58aT, ASTM Standards on Rubber Products, 19th Edition (1960).
- ⁹³ Harris, I. W. E., Polymer Corporation Limited, Private Communication (1952).
- ⁹⁴ Seaman, R. G. and Carlton, C. A., *Rubber World* **140**, 421 (1959).
- ⁹⁵ Anon, *Rubber World*, **144**, 116 (1961).
- ⁹⁶ Anon, R. T. Vanderbilt Co., *The Vanderbilt News*, **27**, No. 1 (1961).
- ⁹⁷ Dorko, Z. J. and Pfisterer, H. A., *Rubber Age* **83**, 105 (1958).
- ⁹⁸ Gelinas, L. P. and Storey, E. B., *Proc. Internat. Rubber Conf.*, Washington (1959) p. 95.
- ⁹⁹ Briggs, G. J., Private Communication to Polymer Corporation Limited.
- ¹⁰⁰ Rooney, H. E., Private Communication to Polymer Corporation Limited.
- ¹⁰¹ Grace, N. S., *India Rubber World* **126**, 633 (1952).
- ¹⁰² Morton, A. A., Magat, E. E. and Letsinger, R. L., *J. Am. Chem. Soc.* **69**, 950 (1947).
- ¹⁰³ D'Ianni, J. D., Naples, F. J. and Field, J. E., *Ind. Eng. Chem.* **42**, 95 (1950).
- ¹⁰⁴ Dinmore, R. P., *Trans. Inst. Rubber Ind.* **28**, 166 (1952).
- ¹⁰⁵ Storey, E. B., Private Communication to Polymer Corporation Limited.
- ¹⁰⁶ Geisler, A. M. and Sayko, A. F., *Ind. Eng. Chem.* **41**, 1751 (1949).
- ¹⁰⁷ Ziegler, K., Holskamp, E., Breil, H. and Martin, H., *Angew. Chem.* **67**, 426 (1955).
- ¹⁰⁸ Kraus, G., Short, J. N. and Thornton, V., *Rubber and Plastics Age* **38**, 880 (1957).
- ¹⁰⁹ Railsback, H. E., Cooper, W. T. and Stumpe, N. A., *Rubber and Plastics Age* **39**, 938 (1958).
- ¹¹⁰ Staveland, F. W., et al., *Ind. Eng. Chem.* **48**, 778 (1956).
- ¹¹¹ Horne, S. E., Jr., Kiehl, J. P., Shipman, J. J., Folt, V. L., Gibbs, C. F., Willson, E. A., Newton, E. B. and Reinhardt, M. A., *Ind. Eng. Chem.* **48**, 784 (1956).
- ¹¹² Hannagan, F. W., *Rubber and Plastics Age* **42**, 166 (1961).
- ¹¹³ Sittig, M., *Petr. Refiner*, **39**, (No. 11), 162 (1960).
- ¹¹⁴ Sarbach, D. V., *Rubber Age* **89**, 283 (1961).
- ¹¹⁵ Mayor, R. H., Saltman, W. M. and Pierson, R. M., *Petr. Refiner* **37**, 208 (No. 11) (1958).
- ¹¹⁶ Smith, W. A. and Willis, J. M., *Rubber Age* **87**, 815 (1960).
- ¹¹⁷ Buckler, E. J. and Harris, I. W. E., *Trans. Inst. Rubber Ind.* **31**, 2 (1955).
- ¹¹⁸ Harris, I. W. E. and Pfisterer, H. A., *Rubber and Plastics Age* **41**, 1527 (1960).
- ¹¹⁹ Storey, E. B., Private Communication to Polymer Corporation Limited (1953).
- ¹²⁰ Fraser, D. F., *Ind. Eng. Chem.* **32**, 320 (1940).
- ¹²¹ Thompson, D. C., Paper presented in the "Symposium on Oil Extension of Rubbers", Brooklyn Polytechnic Institute (1955).
- ¹²² Thompson, D. C., *Rubber Age* **72**, 638 (1953).
- ¹²³ Hartman, J. L. and Thompson, D. C., *Rubber World* **130**, 498 (1954).
- ¹²⁴ Thompson, D. C. and Catton, N. L., *Ind. Eng. Chem.* **42**, 892 (1950).
- ¹²⁵ Whitby, G. S., "Synthetic Rubber" John Wiley and Sons, Inc. (1954).
- ¹²⁶ Adams, R. J., Buckler, E. J. and Wanless, G. G., *RUBBER CHEM. & TECHNOL.*, **23**, 670 (1950).
- ¹²⁷ Adams, R. J. and Buckler, E. J., *Trans. Inst. Rubber Ind.* **29**, 17 (1953).
- ¹²⁸ Fox, T. G. and Flory, P. J., *J. Am. Chem. Soc.* **70**, 2384 (1948).
- ¹²⁹ Private Communication from Esso Research and Engineering Company.
- ¹³⁰ Edwards, D. C. and Storey, E. B., *Trans. Inst. Rubber Ind.* **31**, 45 (1955).
- ¹³¹ Mullins, L., *Trans. Inst. Rubber Ind.* **22**, 235 (1947).
- ¹³² Geisler, A. M., *Rubber Age* **74**, 59 (1953).
- ¹³³ Edwards, D. C. and Storey, E. B., *RUBBER CHEM. & TECHNOL.*, **30**, 122 (1957).
- ¹³⁴ Dunkel, N. L., Smith, W. C. and Zapp, R. L., *Rubber and Plastics Age* **38**, 892 (1957).
- ¹³⁵ Ernst, J. L. and Stuart, S. R., *Proc. Internat. Rubber Conf.*, Washington (1959) p. 38.
- ¹³⁶ Natta, G. and Crespi, G., *Rubber Age* **87**, 459 (1960).
- ¹³⁷ Amberg, L. D. and Robinson, A. E., *Ind. Eng. Chem.* **53**, 368 (1961).
- ¹³⁸ Dingle, A. D., *Rubber World* **143**, 93 (1960).
- ¹³⁹ Amberg, L. O. and Willis, W. D., *Proc. Internat. Rubber Conf.*, Washington (1959), p. 565.
- ¹⁴⁰ Anon, *Rubber and Plastics Age* **40**, 437 (1959).

CARBON BLACK—LATEX MASTERBATCHES

H. J. J. JANSSEN AND K. V. WEINSTOCK

THE GENERAL TIRE & RUBBER COMPANY, AKRON, OHIO

INTRODUCTION

Around 1920, the reinforcement of natural rubber by dispersions of about 20 per cent by volume of extremely small particles of carbon black became established. This gave stocks with improved resistance to tear and abrasion, very suitable for tires, which have made possible the safe, quiet, high speed traffic on land and in the air which we know today. The dispersions were obtained by high shear mixing of carbon black and dry rubber in conventional rubber masticating equipment.

Attempts to mix black with natural rubber in the latex stage were made early and a patent applied for in 1922 by Petersen¹ contains all the essential elements of the processes for filler-latex masterbatching. The following quotation from this patent may be of historical interest: ". . . this invention is based upon the discovery that the rubber content of latex will unite with and coagulate in the presence of a foreign substance, such as carbon black, which has previously been thoroughly dispersed in a suitable liquid medium . . ." . . . " . . . the initial coagulum is ordinarily too high in carbon black content to serve any useful commercial purpose . . ." . . . "While the practice of previously dispersing the carbon black in a liquid can be successfully attained by the use of water alone, a more thorough dispersion of that solid can be attained by adding to the water a suitable quantity of . . . soap, dilute glue or the like. The action of this secondary addition to the water content on the carbon black appears to be analogous to lubrication, whereby the fine particles of carbon black are caused to separate under the influence of agitation, and whereby in their more effectively separated or dispersed state, the intermingling therewith of the solid content of the latex is facilitated . . ."

The bibliography by Braendle² also lists a number of patents applied for shortly afterwards. Several of these patents present an over-optimistic feature when it is claimed that the dried carbon black-latex masterbatch can produce reinforced rubber articles without high shear mixing, whereas it is known from experience in latex technology that such a product is not to any degree comparable in strength to the dry mixed compound and that a latex-masterbatch process can at best deliver to the masticating equipment a premix which can be given a shorter mixing cycle and still result in an extremely well dispersed compound.

Although some advantages for masterbatching carbon black with natural latex would appear to be evident, this process has not been successful. One reason for this is undoubtedly that the producers of carbon black and natural latex are situated in almost antipodes, so this would necessitate extra transport of either carbon black or water over a large distance. But, even rubber

manufacturers close to rubber plantations have not practiced it to any large extent. Possible reasons are:

- a) the variability of rubber content and viscosity of the rubber in natural latex
- b) the difficulty of reducing this viscosity
- c) the absorption of nonrubber constituents by the carbon black and the accelerated degradation of the masterbatch in storage.

Compagnon and Liponski³ have described a semicommercial production of black masterbatch in Indo China which was discontinued.

In the case of SBR synthetic latex, almost none of these disadvantages applies. The rubber and the filler are in many cases produced in close proximity from the same raw materials, petroleum or natural gas. The rubber content and the properties of synthetic latex can be held within close specifications and the amount of nonrubber solids is low. It is, therefore, not surprising to find that carbon black masterbatching with SBR latex was carried out in 1944, soon after the introduction of this rubber. Swart and coworkers⁴ have reported on the first production of an EPC-Hot GR—S Latex masterbatch on a commercial scale as carried out in the Synthetic Rubber Plant in Baytown, Texas by The General Tire & Rubber Company under U. S. Government licence. The carbon black was dispersed in water with surface active agents in order to make the process workable in the available equipment. They found the masterbatch to be equivalent in quality to dry-mixed stocks. The main advantages were found to be an increase in milling capacity by 35 per cent, a reduction in power requirements by 20 per cent and a cleaner operation in the rubber manufacturing plant. Production was switched to Cold SBR and HAF-black as soon as these materials became available. With this combination, however, the latex masterbatch was found to be slightly inferior in road wear resistance to a good dry mix and as a result, the production of "black rubber" decreased steadily from 1949 on. It was not until 1953 when Hulings⁵ announced the development of a nondispersant process in a pilot plant, that the inherent possibility of improving the quality over that of dry mixes was realized. At this time Braendle² was also working on the development of a nondispersant variation of the process. Renewed interest in latex-masterbatching was created and in 1957, production started increasing again. Drogin⁶ lists seven synthetic rubber producers who are offering black masterbatches and it is expected that this year one quarter of all SBR produced in the United States will be in this form.

THEORETICAL DISCUSSION

The problem of explaining why carbon black reinforces rubber has intrigued numerous rubber scientists for over 40 years and progress toward the solution is still slow. The present authors adhere to the view⁷ that the fundamental feature of the reinforcing mechanism is the reversible opening of a weak bond between the carbon black surface and a rubber molecule which is under moderate stress. By allowing relief of stress of highly stressed molecules in this way and thus improving the stress distribution among the elements of the network, this causes the break to occur at a higher average stress and at a higher elongation. Similar stress relief mechanisms can easily be postulated also for the other types of rubber reinforcement: reinforcement by crystallization, by ionic crosslinks and resin reinforcement. Other theories base the reinforcement on strong

bonds between rubber and black⁸ or on a chemical effect of the black surface on the vulcanization reaction⁹. Independent of theory, however, there is general agreement that the degree of reinforcement is determined by the nature of the carbon black surface and that the larger the surface area available, the more reinforcement one obtains, hence the need for small particles. Since the reinforcing action must be distributed evenly throughout the rubber, the need for excellent dispersion arises. The degree of dispersion one can attain with a given carbon black will again depend mainly on the nature of its surface, but the surface properties required may be different from those essential for the reinforcing action. There is no evidence that the treatment which the carbon black receives during latex masterbatching gives any improvement of its surface characteristics, either with respect to reinforcement or to dispersibility. On the contrary, the view is held that any changes caused by the process are likely to have a deleterious effect. Thus the object of the latex masterbatching operation can be described as the production of a mixture of the two ingredients, which is well adapted to further dispersion by conventional masticating equipment and in which the properties of the rubber and the black have not been significantly changed.

SBR latex is obtained as a colloidal dispersion of about 25 per cent by volume of a styrene-butadiene copolymer in water, stabilized by fatty or rosin acid soaps. The water phase contains small amounts of the reaction products of the catalyst, the modifier and the shortstop. The size of the negatively charged particles averages from 60 to 70 μ . The particle size can be increased by creaming, either by adding salts which depress the ionization of the soap or special agents (e.g., alginates) which cause latex particles to adhere to each other. Strong shearing forces will cause some coagulation of the latex, especially at higher temperatures. In the synthetic rubber plants, the latex is first creamed by bleeding in a salt solution at the intake side of the centrifugal pump which forces the latex into the coagulation tank, where a pH of 2.5 to 3 is maintained by continuous addition of sulfuric acid, and from which the coagulated crumb overflows to the next piece of equipment. The creaming step cannot be dispensed with for otherwise it is impossible to obtain a crumb of the right particle size for efficient filtering, washing and drying.

The reinforcing grades of carbon black consist of extremely small particles of fairly pure carbon which are nearly always spherical with a relatively smooth surface. The average size is 15 to 30 μ . Two varieties are distinguished by method of manufacture, the channel blacks and the furnace blacks. The former have the higher volatile content, the latter the higher content of ash and oil. Most of these impurities appear to be located at the surface of the particles. Studebaker¹⁰ gives the following values for the concentration of four components, which may be considered contaminants, for two typical reinforcing blacks.

	%O	%H	%S	%Ash
Easy Processing Channel	2.9-3.5	0.6-0.75	0.2	0.02
High Abrasion Furnace	0.5-1.0	0.27-0.34	0.6	0.3

A third variety—the thermal blacks—is not manufactured in the reinforcing range of particle size. Thermal blacks may contain about 0.4 per cent hydrogen and 0.3 per cent ash, with practically no oxygen or sulfur.

The two most important noncarbon constituents of carbon black are hydrogen and oxygen. Most of the hydrogen atoms are bonded to carbon, either as

aromatic ring hydrogen at the edges of graphitic crystallites or in the non-oriented carbon¹¹. A small portion of the hydrogen is bonded to oxygen, either as carboxyl or phenolic hydroxyl at the particle surface^{12, 13}. Part of the remaining oxygen may be present in quinone and semiquinone structures again at the particle surface^{14, 15, 16, 17}. For more details the reader is referred to the review on carbon black chemistry by Studebaker¹⁰.

In view of the large variety of chemical structures at the particle surface one may safely postulate that a wide spectrum of bonding forces to a neighboring particle is theoretically possible; starting with the strength of the bond between two particles welded together during their formation, through primary bonds, hydrogen bonds, down to the weakest, long range physical attractions.

Carbon black is obtained as a loose powder of bulk density 0.05. To ease transportation and handling, it is pelletized to a bulk density of about 0.4. Since the true density¹⁸ is 1.8 to 2.1 pelletizing reduces the amount of air from about 97 to about 80 per cent by volume. Pelletization is carried out by agitating the black under compression. The presence of water or aqueous solutions of surface active agents can aid the process. If the densification is carried too far, the pellets may become too hard and too strong for easy dispersion. Dannenberg and coworkers¹⁹ have shown the loss of tensile strength and elongation of dry mixed stocks that accompanies increased bulk density of the black. It is evident that agitation under compression is a condition that exists in an internal mixer and during incorporation of the black in this machine a small portion is converted into hard beads, which do not disperse and which can be seen with a light microscope in thin sections of the uncured and cured stocks²⁰. To minimize this, black is added to the internal mixer "over the ram" to allow it to enter the mixing chamber in a slow stream, so that no large amount is exposed to the densifying conditions at any moment. Hess²¹ has shown that large, dense agglomerates are undesirable in cured rubber because tears or cracks are liable to be initiated inside them.

The low bulk densities of carbon black are made possible by its tendency to form chains bonded by the surface forces between individual particles. It exists as aggregates, containing millions of particles, constructed of these chains. That this structure is very open can be demonstrated easily by gently shaking pelletized black with phosphoric acid of density 1.7 when most of the beads will sink. The tendency to form these open structures is measured as a resistance to densification in the "oil absorption" test. Oil is gradually added to a weighed amount of black under moderate spatulation until the mixture has just been worked into a single, stiff ball. Sweitzer and Goodrich²² have suggested a graphical method of calculation that produces a "structure index" which is independent of particle size.

The oil absorption of a normal HAF black is about 1.2 ml/g which amounts to about 65 volume per cent of oil at the endpoint. That formation of structure is related to the surface oxygen content is indicated by the fact that thermal blacks, even with particle sizes in the reinforcing range²³, have oil absorption values of less than one-third of the above values, thus approaching the theoretical minimum—the space between closely packed spheres. The oil absorption of reinforcing blacks can be reduced almost to this level by graphitization, which removes the surface oxygen, and by ball milling, which increases the surface oxygen²⁴.

One can speculate that the greatest resistance to densification will be given by a black in which the particles can form strong bonds at only two or three

locations on each particle surface in contrast to, on the one hand, blacks that can only form weak bonds and would densify easily and, on the other hand, blacks that can form strong bonds all over the surface and could be compacted to very stable, dense beads. Studebaker¹⁰ has recommended measurement of the apparent specific volume of dry blacks under 50 atm. pressure as an alternative to the oil absorption test.

That the surface forces of carbon black may depend on the medium can be deduced from the heats of immersion in various solvents measured by Kraus²⁴. In hexane, all blacks give values around 100 ergs/cm² but in water, a graphitized black gives 31 ergs/cm², furnace blacks 40 to 60 ergs/cm² and a channel black 84 ergs/cm². The carbon black-latex masterbatching process can be visualized as the problem of black structure in three media—first air, then water and finally a hydrocarbon—rubber. Since adsorbed films can destroy attractive surface forces, the use of dispersants may have a decisive effect.

The first step in the dispersant processes starts with dry micropulverization of the black to break up the large aggregates—pellets or beads—into smaller ones. This is accompanied by a decrease in the bulk density. The dry ground black is then dispersed by mechanical agitation in water containing an anionic surface active agent, usually a polyalkylnaphthalene sulfonate or a lignin sulfonate. Generally, some alkali is also added. In this way, a very fast and efficient breakdown of carbon black aggregates takes place and jet-black, free-flowing slurries are obtained with as high as 20 weight per cent of carbon black. Anions of the dispersant are absorbed on the carbon black surface and the resulting negative charges inhibit reagglomeration. If these slurries are dried with or without acidification one obtains very hard, shiny crusts. The degree of disaggregation, which is never even near completion, can be followed by viscosity or light transmission measurements²⁵. A new piece of equipment, the Coulter counter²⁶ allows the aggregates to be counted electrically by employing the change in conductivity when a particle passes through a small orifice. By variation of orifice diameters the particle size distribution can then be obtained. Adams and Howland²⁷ have calculated that in a well-stabilized slurry, the size of the aggregates has been reduced to about the size of rubber particles in a standard SBR latex.

In the nondispersant processes, the object appears to be to give the minimum of aggregate breakdown that is feasible. This results in greyish slurries which at a concentration of 5 per cent by weight carbon black are of a soggy consistency. Slurries with more than 8 per cent by weight are too thick to handle in pumps and pipe lines. Dannenberg and Seltzer²⁸ have shown that the rate of wetting of dry carbon black is reduced by traces of benzene extractable material and by micropulverization to a lower bulk density. Very fast wetting is obtained in a fluid energy mill²⁸, ²⁹ with high temperature steam which is later condensed on the carbon black.

Reich and Vold³⁰ have studied the flocculation of carbon black in water as a function of time, concentration and intensity of agitation with the aid of light transmission measurements. In agitated suspensions, they found an equilibrium between formation and destruction of aggregates. The average aggregate size always increased with increasing concentration and with decreasing speed of agitation. By leaving a suspension prepared with high speed stirring at rest, the equilibrium could be "frozen in" as the average floc size remained almost constant for long periods. Mild agitation would then start growth of the flocs again. One would expect in an aggregate subjected to

mechanical forces that the weakest bonds between particles would break first and in the case of a dynamic equilibrium one would obtain, with time, a stronger aggregate, but there is no evidence to this effect.

Channel black is more easily dispersed in water than furnace black because of the more hydrophilic character of its surface. Channel black dispersions are acidic and the decrease of the pH is in proportion to the amount of volatile oxygen^{31, 32}. The acidity can be explained by assuming dissociation of hydrogen ions from carboxyl or phenolic hydroxyl groups. This would leave a negative charge on the black particles.

Furnace black slurries are slightly alkaline. This is partly due to the presence of soluble, alkaline ash and Adams and Howland²⁷ have shown that the major part of this ash is removed in latex masterbatching, causing the stocks to cure somewhat slower than corresponding dry mixes. Wiegand³¹ found that a channel black, which contained no ash and which had been heat treated to remove all oxygen, also gave alkaline slurries. To explain this, Studebaker¹⁰ suggested that polycondensed aromatic rings would have electron donor behavior and might be expected to absorb hydrogen ions. This would give a positive charge to the black.

The second step is the mixing of latex and carbon black slurry. Emulsions of extender oils and antioxidants can be added at the same time. In the case of the dispersant processes with large amounts of stabilizers, the mixing of the two stable colloidal systems with negatively charged particles should have no colloidal effects—only a slow exchange of dispersants is to be expected. In the case of the nondispersant types, the carbon black can absorb soap fast as shown by the experiments of Maron and coworkers³³. Desorbing of soap from the latex particles will lower the stability of the latex and in this way carbon black can be used as a creaming agent and salt can be dispensed with in the coagulation. The absorbed soap may cause some of the bonds between black particles to break. If the carbon black comes to a state of dynamic re-aggregation, it is possible that latex particles will be trapped in black agglomerates. After coagulation and drying, these will form beads reinforced by a small amount of rubber and it is a known fact that such beads can not be dispersed in subsequent processing. To eliminate this danger, the contact time of latex and black before coagulation is kept as short as possible. The absorptive powers of carbon black may enter the picture here. If a thiocarbamate has been used to shortstop the latex, absorption on the carbon black will carry it over into the masterbatch as such or as its reaction products and this will produce an activation of the rate of vulcanization of the final product.

The next step—the coagulation—is critical. If the acid is added slowly to the latex-black slurry, the first precipitate will contain a very high concentration of carbon black and may give rise to the formation of the undispersible black beads mentioned above. Petersen¹ had already noticed this and Adams and coworkers³⁴ confirmed that precipitates with 40 to 50 per cent of black by weight are responsible for poor vulcanizate quality, and Dannenberg and coworkers³⁵ observed that the formation of such precipitates could be suppressed by use of the correct amount of the right type of dispersant. Swart and coworkers⁴ found that the coagulation techniques developed for latex alone would only lead to inferior quality when practiced with the blend of latex and black slurry—the carbex. The creaming step had to be left out and an excess of salt and sulfuric acid added rapidly to the mixture under high speed stirring. This was termed "shock" coagulation. Later work led to development of the

"reverse" coagulation in which the carbex is added to the excess of salt and acid. The nondispersant processes with blending in a steam jet use this technique also for the jet is usually situated above the coagulation tank and the carbex is blown down into the dilute acid.

When powerful dispersants of the polyalkylnaphthalene sulfonate type are used filter-passing "fines" may be formed. Adams and coworkers³⁴ were able in most cases to bond these fines into recoverable particles by adding polyamines.

The ideal coagulum could be one in which black agglomerates, filled with pure water, are completely coated with rubber. Larger agglomerates have a smaller total surface and should hence be easier to encapsulate with a given amount of rubber.

In this stage, the unencapsulated carbon black can absorb salt and acid and according to Adams and Howland³⁷ will retain 90 per cent of any dispersant used. Unless these are washed out, their presence may be detrimental to the electrical properties and water resistance of the compounds. For the non-dispersant types, where one can also dispense with the salt, this problem is of less importance. After filtering, the crumb contains about 30 per cent of water or more.

Because the carbon black has increased both the stiffness and the porosity of the coagulum, a large portion of the water can be squeezed out mechanically and work to develop radically new equipment which utilizes this property is in progress^{36, 37, 38}. A further impetus to these experiments is given by the consideration that the mechanical energy expended in this direction is not wasted, as it would be for rubber alone, but may contribute to the black dispersion and thus take part of the load off processing equipment further along the line.

The development of new masticating equipment for rubber³⁹ is in many cases tied in also with black masterbatch dried in the conventional manner, for one of the usual directions for improvement is towards a design with continuous feed and small holdup. If such a machine is fed white rubber and dry black one may expect difficulties in keeping the rubber to black ratio reasonably constant, but black masterbatch would be the ideal raw material. The same applies to pelletization of rubber and if the mechanics of extrusion could be improved to permit handling of stiffer materials, one might obtain large advantages in handling and storage in a rubber manufacturing plant as Drogin⁶ has pointed out. TeGrotenhuis⁴⁰ has obtained a patent on a process based on the pelletization of wet crumb. The above will suffice to show why the black-latex masterbatch process is an integral feature of many development projects in the rubber industry.

The last step in the process is the drying of the crumb. This is usually carried out in a tunnel drier with a blast of hot air. The presence of carbon black improves this step in several ways. The crumb is harder and less tacky; it is also more porous and has higher heat conductivity. Thus, the efficiency of the operation is improved, if calculated on the basis of water removed or wet masterbatch throughput. However, the rubber throughput has decreased slightly, so that a synthetic rubber producer who switches to masterbatch production will need an increase in drier capacity. Since the highest temperature during the process is reached in this stage, it is here that the greatest danger of a change in the rubber properties or in the nature of the black surface arises. Contributing factors may be the absorption of traces of acid or other materials on the black and its catalytic activity. The drying is, therefore, sensitive to temperature control and a maximum temperature of 170° F in the crumb should

be rigorously prescribed. Stickney and coworkers⁴¹ were able to show that heating a black-polybutadiene masterbatch at 180° F or higher temperatures gave an increase in the "bound rubber" or "carbon gel" content. This test provides a measure of the insolubilization of the rubber. If parts of the rubber become crosslinked to such a degree that carbon black particles can no longer be incorporated therein by mechanical shear, the vulcanized stock will contain extremely weak, pure gum regions.

The oxygen content of many carbon blacks increases when they are exposed to air at higher temperatures. The effect of this on a dry mixed stock is to reduce the rate of cure and depress dispersion²⁸. Smith and coworkers⁴² investigated the reaction of water with carbon black at temperatures from 25 to 200° C. The presence of a carbon-oxygen surface complex greatly increased the amount of a reaction, which produced hydrogen, hydrogen sulfide and carbon dioxide as the main gaseous products.

The hot, dry crumb is compressed in a hydraulic press to bales that are sufficiently nontacky to be shipped without wrapping. The bulk density of the final product is close to 1.1. Compared to the bulk densities of the raw materials of 0.9 to 0.4 for rubber and black respectively, this shows the savings in space during shipping and storage made possible by the process. It also indicates that the product contains only about 5 per cent by volume of air, most of which is present in bubbles visible to the naked eye. Thus, most of the space between carbon black particles has been filled with rubber. If this has taken place without densification of the carbon black structure, the gross dispersion should be good. 80 per cent by volume of air has been replaced by 80 per cent by volume of rubber and all that remains is to destroy the black structure and incorporate the other compounding ingredients. One may wonder at which stage of the process the rubber entered the black agglomerates. Dannenberg³⁵ speculates that in the dispersant processes this takes place during creaming or coagulation, but it is hard to see how latex particles could diffuse into the large, water-filled aggregates in the extremely short time available in the nondispersant processes. It must then have taken place during drying and/or baling. The rate at which the rubber will flow into the aggregate channels as the water leaves will depend on the viscosity of the rubber, the temperature, the openness of the structure and the surface tensions among the three components. Formation of a partial vacuum inside encapsulated aggregates as they cool in the baling press may be a contributing factor.

It is customary to test the Mooney viscosity of black masterbatches after mill massing and again after a short cycle in a laboratory internal mixer. This gives some indication of the power load to be expected in a factory internal mixer and of the processibility of the finished compound.

A test which has proven itself to be valuable is the determination of the carbon gel content according to the method used by Sweitzer and coworkers⁸ on a sample which has been mill massed on a cold, open mill. Good batches generally give values from 5 to 10 per cent carbon gel in this test and deterioration due to excess process temperatures, contamination or other causes shows up in an increase above this level. In a few cases, the test cannot be carried out, because the masterbatch gives up free black to the solvent, but such batches in our experience have always been of excellent quality.

In the past, black masterbatches have been examined for "crocking", the tendency to produce a black smear on paper, but it is now evident that this test has little meaning because free carbon black in itself is not detrimental.

After further dispersion of the black in an internal mixer and addition of the other compounding ingredients, the finished compound is submitted to the standard physical testing procedure. Good dispersant masterbatches give physical properties comparable to those of the analogous dry mixed stocks. However, extensive testing has shown that in the case of the HAF-SBR masterbatch there is a deficiency of about 5 per cent in road wear resistance. A tendency has been observed in some cases for the dispersant masterbatches to show higher modulus, permanent set, tear resistance and electrical conductivity. This suggests that the chain structure of the black has persisted to some degree in these stocks.

Nondispersant masterbatches of good quality show an increase in tensile strength and abrasion resistance together with a decrease in permanent set and electrical conductivity when compared with dry mixed stocks. With HAF-SBR masterbatches the differences is not large (e.g., 300 psi in tensile strength or 10 per cent in road wear) and it takes careful operation to detect the effect. It is, therefore, easier to qualify a masterbatching operation when carried out with blacks which are difficult to disperse in SBR by dry mixing, because of small particle size or low structure index. In these cases, nondispersant masterbatching can produce the quality expected from these blacks by analogy with their behavior in natural rubber. The greatest improvement in properties has been shown by Sweitzer²³. His data indicate an increase of more than 1000 psi in tensile strength and 100 per cent in elongation at the same hardness and modulus level for three special reinforcing blacks of low structure index in oil-extended SBR.

In recapitulation, it can be said that the object of the carbon black latex masterbatching processes is to prepare a mixture of rubber and carbon black, which is well adapted to further dispersion by masticating equipment. One requirement for this is that the carbon black structure should not have been densified. Another requirement is believed to be the absence of black agglomerates containing a small amount of rubber particles.

Both requirements can be satisfied (1) by operating with the lowest degree of breakdown of carbon black that will give slurries which can still be handled and (2) by reducing the contact time of latex and black before coagulation to the minimum. This has led to the development of the nondispersant processes which operate continuously with high rates of material flow. It is a fortunate coincidence that this very economical way of operation has also yielded the highest quality in the products.

TECHNICAL DISCUSSION

It will be apparent from the preceding chapter that the technology of black-latex masterbatch production cannot be considered as finalized and further developments in methods of operation, equipment design and plant layout are to be expected. At present, the production is carried out in plants that have been designed primarily for the production of "white rubber" and to which facilities for storage, handling and latex-blending of carbon black have been added later and one does not get the impression that any two plants are operating with exactly the same procedures. The best way to present the technical aspects of the process is, therefore, in our opinion, to give a list of equipment which has been used successfully and several flow sheets.

EQUIPMENT

1. *Dry grinding.*—Of the numerous machines for dry grinding, two have been mentioned in connection with the carbon black-latex masterbatch process: The Mikro-Pulverizer⁴³—a hammermill—and the Fitzmill⁴⁴—a knife mill.

2. *Wet grinding.*—Dry ground black can be incorporated into an aqueous solution of a dispersant by agitation with a high-speed, air-driven stirrer. This has been carried out as a continuous operation (Figure 1), which required continuous weighing of black and metering of solution, but also in a semicontinuous fashion. In this method, two identical units are used and while in the first one a weighed amount of black is run through the grinder into a known volume of solution, the finished slurry in the second unit is being run out for blending with a known volume of latex.

It has been reported⁶ that the Mikro-Pulverizer⁴³ and the Fitzmill⁴⁴ have also been used for wet grinding.

Colloid mills, e.g., the Charlotte mill⁴⁵, which depend for their grinding action on the high hydraulic shear between a grooved rotor and stator, have been used for the reduction of the agglomerate size of stabilized slurries.

The simple beating action of a spiked shaft rotating at 4000 rpm inside a cylinder with baffles has been used to break up carbon black pellets in water on the Pilot Plant scale. The apparatus has been named "bead disperser"⁴⁶.

3. *Steam grinding.*—This is carried out in "fluid energy" mills, characterized by a violently turbulent stream of gas at sonic or supersonic velocity traveling a closed path. The material to be ground is forced into the grinding zone and the smallest particles are taken out by a classifying action. This gives a narrow distribution of particle sizes in the product. With carbon black the fluid used is steam and slurries can be made by simply spraying the outlet stream with cold water, provided that the air, which was originally held in the black is given a means to escape.

Of the half-dozen fluid energy mills available, at least two have been used for carbon black grinding: the Jet-O-Mizer²⁸ and the Micronizer²⁹. Both are suitable for nondispersant slurry preparation.

4. *Blending.*—In the dispersant processes, the latex and the stabilized black slurry are simply run into a blending tank together. In the first nondispersant process reported⁵, the latex and the slurry were fed to a steamjet. The violently turbulent conditions inside this simple piece of equipment gave practically instantaneous mixing. The "bead disperser" has been used for blending on a Pilot Plant scale⁴⁷. The Entoleter⁴⁸, a continuous, high speed, centrifugal mixer with impact action, has also been used for this purpose.

5. *Coagulation.*—Customarily the "carbex" is run into the coagulation tank to which acid and if necessary salt solution are added automatically. The pH is kept at the required level by remote control. Then the vortex produced by a high speed stirrer causes the coagulated crumb to overflow to a conversion tank where it is stirred long enough for all the soap to react with acid. The crumb is then filtered on shaker screens and washed with water.

6. *Expelling of water.*—After washing, the crumb is usually run over a rotary filter. Vacuum and press rolls can be used to improve the water removal. Further reduction in the amount of water can be given by machines using the extruder principle, e.g., the Anderson expeller⁴⁹. In this machine, a compressing screw rotates inside a slotted housing and an adjustable cone baffle at the discharge end regulates the pressure built up. The slots widen

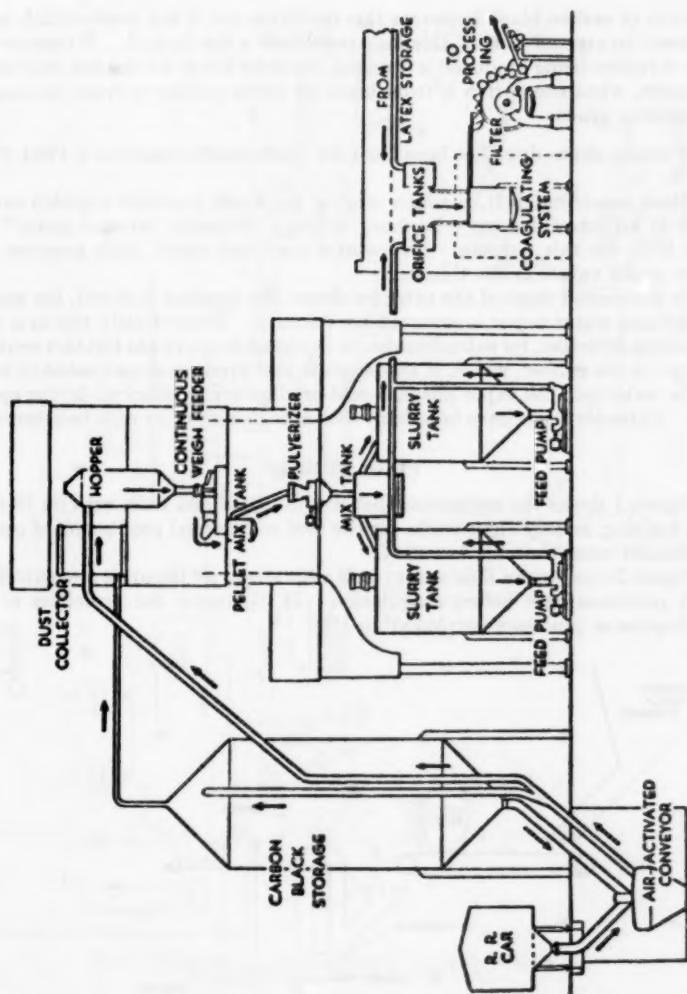


FIG. 1.—Equipment added to an existing SBR plant for the first commercial production of carbon black-latex masterbatches (1944). (Courtesy of Blaw-Knox Company, Pittsburgh, Pa.)

outward and cannot be plugged up by pieces of crumb which pass through. The first stage of the extruder-driers operates on the same basis.

Squeeze rolls with a friction action have also been employed^{50, 51}.

7. *Drying*.—The conventional method of drying is technically the least satisfactory operation in rubber production. Tunnel driers have a tendency to be gummed up by degraded rubber and have to be cleaned regularly and it takes a crew with special equipment one week to clean a single unit. The

presence of carbon black improves this condition but if the masterbatch has a tendency to give off "fines" this may constitute a fire hazard. Whenever the type of rubber being produced is changed, the drier has to be cleaned, especially, of course, when the switch is from black to white rubber or from staining to nonstaining grades.

A rotary drum drier has been used for black masterbatch on a Pilot Plant scale⁶¹.

Black masterbatch from which most of the water has been expelled can be dried in an internal mixer—Banbury drying. A special internal mixer⁶² has been built for this purpose. Its features are: high speed, high pressure and water outlet valves in the throat.

In the second stage of the extruder driers, the housing is closed, the rubber heated and water vapor is removed by vacuum. Theoretically this is a very promising direction, for extruders can be designed to move gas bubbles counter-current to the rubber, which, if temperature and pressure are adjusted to bring all the water into the vapor phase, would produce a very efficient drying operation. Extruder driers have been built with a single screw³⁷ or with twin screws³⁸.

FLOW SHEETS

Figure 1 shows the equipment that was designed and built with its 70-foot-high housing, in only eight weeks for the first commercial production of carbon black-latex masterbatch^{63, 4} in 1944.

Figure 2 combines a fluid energy mill with steam jet blending and extremely short residence time before coagulation. It illustrates the principles of the nondispersant processes developed⁵ in 1953.

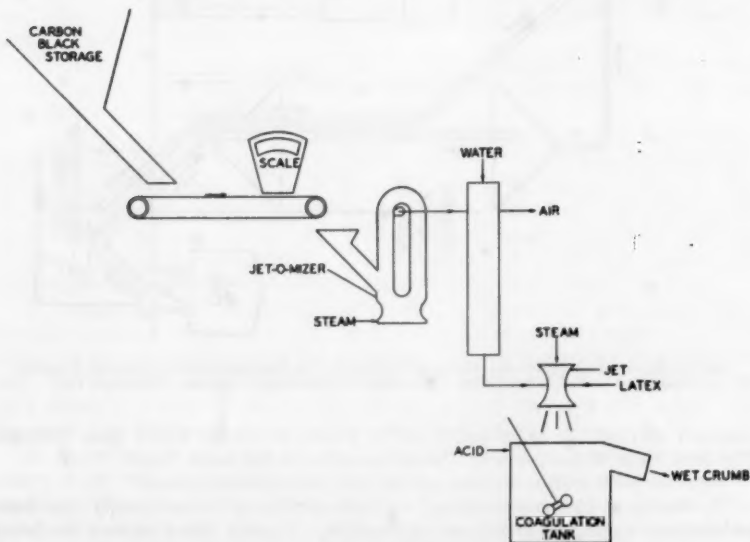


FIG. 2.—Flow sheet for production of nondispersant masterbatches with fluid energy grinding and steam jet blending.

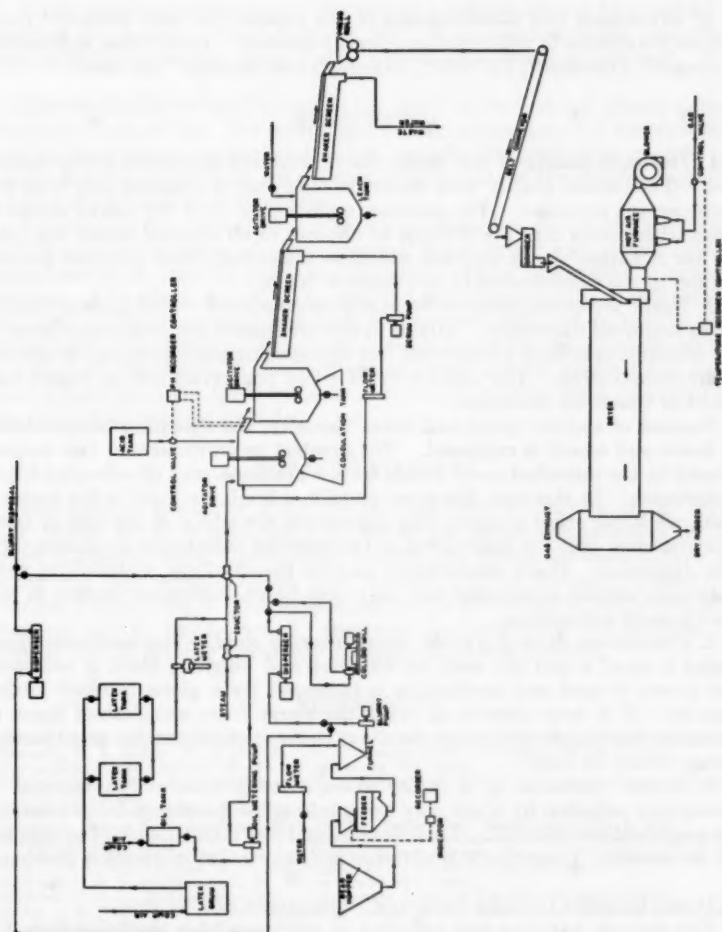


FIG. 3.—Flow sheet of Pilot Plant (1959). (Courtesy of Columbian Carbon Company, New York, New York.)

Figure 2 is the schematic diagram of an actual Pilot Plant operation⁵¹ which comprises bead dispersers, a colloid mill, squeeze rolls and a rotary drier as novel features made public in 1959.

CONCLUSION

The steady increase in production of black latex masterbatches over the past three years⁵⁴ makes it appear probable that the process has become firmly established the "second time around", and its potential value in various development projects promises even greater importance in the future. The following

list of advantages and disadvantages of the process has been compiled from many of the articles to which we have already referred. In addition, statements by Drogin⁶, Forrester⁵⁵, LaPorte⁵⁶, Malone⁵⁷, and Samuels⁵⁸ are used.

ADVANTAGES

1. *Improved quality of tire stocks due to improved dispersion of the carbon black.*—The highest quality with respect to road wear is obtained only with the nondispersant processes. The greatest improvement over dry mixed stocks is shown with blacks that are difficult to disperse in an internal mixer, e.g., the new low structure blacks, and this will allow the carbon black producer greater freedom in the development of new types of black.

2. *Easier processing in the rubber manufacturing plant.*—This again is mainly due to improved dispersion. Mixing cycles are shorter and less power is used. The extrusion operation is improved, less reprocessing and less trouble in setting up are encountered. The uniformity of cured properties and of profile and weight of treads are increased.

Because of shorter cycles and lower viscosity, the operating temperatures are lower and scorch is repressed. The greatest improvement in this respect is found in the manufacture of treads from a nondispersant oil-extended black masterbatch. In this case, the shear given in a 3 minute cycle in the internal mixer, while the other compounding ingredients are added as dry mix or latex masterbatches, plus the shear given in the extruder is sufficient to obtain complete dispersion. Black masterbatch may be the ideal raw material for new, continuous mixing equipment and may also be an important feature in the trend toward automation.

3. *Cheaper operation of a rubber manufacturing plant.*—The warehouse space needed is smaller and the need for handling and weighing black is removed. Less power is used and production is increased for a given internal mixing capacity. If it were possible to make the slurry from unpelletized black in the carbon black plant and pump the slurry to the synthetic rubber plant further savings would be made.

4. *Cleaner operation of a rubber manufacturing plant.*—The removal of atmosphere pollution by black may bring intangible benefits in labor relations and neighborhood goodwill. Less cleaning and less maintenance of equipment will be needed. Loose black is abrasive and may cause lubrication problems.

It will be easier to make black and white stocks side by side.

The storage, handling and weighing of black has been displaced from the rubber manufacturing plant to the synthetic rubber plant. Here, however, it is easier to operate with a closed system and the weighing operation can be continuous.

DISADVANTAGES

To the consumer.—1. Bales for use on a mill or small internal mixer must be cut.

2. The peak power on these machines is higher than with a "white rubber"—dry black mix.

3. Some masterbatches cure somewhat slower than corresponding dry mixes, whereas others are decidedly faster curing. Thus, the products from various suppliers are less interchangeable than white rubbers.

To the producer.—Apart from the cost and trouble caused by the need for handling and storage of carbon black, the process requires larger amounts of water and increased drier capacity if conventional techniques are used.

The decision of whether or not to use black masterbatch is almost entirely a matter of economics. For each situation, the advantages and disadvantages have to be weighed against each other carefully by production experts. In many cases, the discussions are between departments of the same company or between closely affiliated companies.

A portion of the production is sold to smaller rubber manufacturers without SBR production facilities who have received the principle warmly and used the masterbatches in steadily increasing amounts. Some production is exported overseas. The advantage of saving space in shipping obtained in this case will disappear as the importing countries become self sufficient in carbon black production. The future of the process depends on such economic considerations as well as on the results of the development work now in progress and on the value placed upon the improvements in product quality, plant operation and cleanliness that may be obtained.

ACKNOWLEDGMENT

The authors gratefully acknowledge their indebtedness to G. H. Swart, A. J. Beber, H. R. Wilson and J. J. Devitt for valuable suggestions, to Lois Brock, Catherine Burg, Grace Corey and Phyllis Kogele for assistance in preparing the manuscript and to The General Tire & Rubber Company for permission to publish it. All statements in this article have been found in the literature and do not necessarily represent the opinions of the authors, The General Tire & Rubber Company, or other employees thereof.

REFERENCES

- 1 Petersen, A. H. (assigned to Kelly-Springfield Tire Company), U. S. 1,611,278 (December 21, 1926).
- 2 Braendle, H. A., *Rubber World* 136, 835 (1957); *RUBBER CHEM. & TECHNOL.* 31, 147 (1958).
- 3 Compagnon, P. and Liponaki, M., *Rev. gén. caout.* 29, 272 (1952).
- 4 Rongone, R. L., Frost, C. B. and Swart, G. H., *Rubber Age* 55, 577 (1944); *RUBBER CHEM. & TECHNOL.* 18, 130 (1945).
- 5 Hulings, C. M., *India Rubber World* 128, 91 (1953).
- 6 Drogin, L., "Latex Masterbatching", *Proc. Internat. Rubber Conf.*, Washington, 1959, p. 476.
- 7 Janssen, H. J., "Discussion of the Physical Aspects of the Reinforcement of Elastomers by Carbon Black", Presented before the Southern Rubber Group, Houston, Texas Meeting, February 21, 1958.
- 8 Schweitzer, C. W., Goodrich, W. C. and Burgess, K. A., *Rubber Age* 65, 651 (1949).
- 9 Studebaker, M. L. and Nabors, L. G., *Rubber Age* 85, 984 (1959).
- 10 Studebaker, M. L., Rubber Reviews for 1957, *RUBBER CHEM. & TECHNOL.* 30, 1400 (1957).
- 11 Austin A. E., "Crystal Structural Properties of Carbon Blacks", presented at the Third Conference on Carbon, University of Buffalo, (1957).
- 12 Villars, D. S., *J. Am. Chem. Soc.* 70, 3655 (1948).
- 13 Studebaker, M. L., Huffman, E. W. D., Wolfe, A. C. and Nabors, L. G., *Ind. Eng. Chem.* 48, 162 (1956).
- 14 Garten, V. A. and Weiss, D. E., *Australian J. Chem.* 8, 68 (1955).
- 15 Garten, V. A. and Weiss, D. E., "Functional Groups in Activated Carbon and Carbon Black with Ion and Electron Exchange Properties", presented at the Third Conference on Carbon, University of Buffalo, (1957).
- 16 Garten, V. A. and Weiss, D. E., *Res. Pure and Appl. Chem. (Australia)* 7, 69 (1957).
- 17 Hallum, J. V. and Drushel, H. V., *J. Phys. Chem.* 62, 110, 1502 (1958).
- 18 Rossmann, R. P. and Smith, W. R., *Ind. Eng. Chem.* 35, 972 (1943).
- 19 Dannenberg, E. M., Jordan, M. E. and Stokes, C. A., *Rubber World* 122, 663 (1950).
- 20 Sweitzer, C. W., Hess, W. M. and Callan, J. E., *Rubber World* 138, 869 (1958); 139, 74 (1958).
- 21 Hess, W. M., "The Analysis of Pigment Dispersion in Rubber by Means of Light Microscopy, Micro-radiography and Electron Microscopy". Presented at ACS Rubber Division Meeting, Louisville, Ky., April, 1961.
- 22 Sweitzer, C. W. and Goodrich, W. C., *Rubber Age* 55, 469 (1944).
- 23 Sweitzer, C. W., *Rubber Age* 87, 269 (1961).
- 24 Kraus, G., *J. Phys. Chem.* 59, 343 (1955).
- 25 Dannenberg, E. M. and Seltzer, K. P., *Ind. Eng. Chem.* 43, 1389 (1951).
- 26 Coulter Industrial Sales Company, Elmhurst, Illinois.
- 27 Adams, J. W., and Howland, L. H., "Latex Masterbatching", in *Synthetic Rubber* edited by G. S. Whitby, New York and London, 1954.

- ²⁸ Fluid Energy Processing and Equipment Company, Philadelphia, Pennsylvania.
- ²⁹ Sturtevant Mill Company, Boston, Massachusetts.
- ³⁰ Reich, I. and Vold, R. D., *J. Phys. Chem.* **63**, 1497 (1959).
- ³¹ Wiegand, W. B., *India Rubber World* **96**, 43 (1937); *RUBBER CHEM. & TECHNOL.* **11**, 187 (1938).
- ³² Cines, M. R., *Rubber Age* (N. Y.) **69**, 183 (1951).
- ³³ Maron, S. H., Bobalek E. G. and Shiu-Ming, F., *J. Coll. Sci.* **11**, 21 (1956).
- ³⁴ Adams, J. W., Messer, W. E. and Howland, L. H., *Ind. Eng. Chem.* **43**, 754 (1951).
- ³⁵ Dannenberg, E. M., Hagopia, E., Hall, J. P., Jr. and Medalia, A. I., *Trans. Inst. Rubber Ind.* **37**, 1 (1951).
- ³⁶ Hale and Kullgren, Inc., Akron, Ohio.
- ³⁷ National Rubber Machinery Company, Akron, Ohio.
- ³⁸ Welding Engineers, Incorporated, Norristown, Pennsylvania.
- ³⁹ Juve, A. E. Beatty, J. R. and Cline, R. H., "The Rotomill—A Continuous Mixing Device", *Proc. Internat. Rubber Conf.*, Washington, (1959), p. 1; *RUBBER CHEM. & TECHNOL.* **33**, 98 (1960).
- ⁴⁰ TeGrotenhuis, T. A. (assigned to The General Tire & Rubber Company), U. S. 2,538,809 (1951).
- ⁴¹ Stickney, P. B., McSweeney, E. E., Mueller, W. J. and Palinchak, S. T., *RUBBER CHEM. & TECHNOL.* **31**, 369 (1958).
- ⁴² Smith, R. N., Pierce, C. and Joel, C. D., *J. Phys. Chem.* **58**, 298 (1954).
- ⁴³ Pulverizing Machinery (Co.) Division of Metals Disintegrating Company, Summit, New Jersey.
- ⁴⁴ W. O. Fitzpatrick Company, Chicago, Illinois.
- ⁴⁵ Chemicolloid Laboratories, Incorporated, Garden City Park, New York.
- ⁴⁶ Braendle, H. A., Heller, G. L. and White, J. W., *Rubber Age* **84**, 431 (1958).
- ⁴⁷ Braendle, H. A., *Rubber World* **136**, 835 (1957).
- ⁴⁸ Entoleter Division, Safety Industries, Incorporated, New Haven, Connecticut, *Chem. Processing* **20**, 168, (1957).
- ⁴⁹ V. D. Anderson Company, Cleveland, Ohio.
- ⁵⁰ TeGrotenhuis, T. A. and Frost, C. B. (assigned to The General Tire & Rubber Company), U. S. 2,441,090 (1948).
- ⁵¹ Heller, G. L., White, J. W. and Braendle, H. A., *Rubber Age* **85**, 605 (1959).
- ⁵² Farrel-Birmingham Company, Incorporated, Ansonia, Connecticut, *Rubber World* **140**, 205 (1959).
- ⁵³ Blaw-Knox Company, Pittsburgh, Pennsylvania, *Rubber Age* **55**, 73 (1944).
- ⁵⁴ Ruebensaal, C. F., *Rubber and Plastics Age* **40**, 1044 (1959).
- ⁵⁵ Forrester, R. A., "The Production of Dispersant Type Black Masterbatch", Presented before the Southern Rubber Group, St. Petersburg, Florida, Meeting, June 5, 1959.
- ⁵⁶ LaPorte, R., "The Use of Black Masterbatch in Compounding", Presented before the Southern Rubber Group, St. Petersburg, Florida, Meeting, June 5, 1959.
- ⁵⁷ Malone, E. L., *Rubber World* **141**, 701 (1953).
- ⁵⁸ Samuels, M., "The Production of Non-Dispersant Type Black Masterbatch", Presented before the Southern Rubber Group, St. Petersburg, Florida, Meeting, June 5, 1959.

RECENT DEVELOPMENTS IN SYNTHETIC RUBBER LATEX

L. H. HOWLAND AND R. W. BROWN

RESEARCH AND DEVELOPMENT LABORATORIES, NAUGATUCK CHEMICAL DIVISION,
UNITED STATES RUBBER COMPANY, NAUGATUCK, CONNECTICUT

CONTENTS

	PAGE
I. Introduction.....	1502
II. Latex types.....	1503
A. Styrene-butadiene (SBR) and related latexes.....	1503
1. Types.....	1504
a. "Hot" latex.....	1504
b. "Cold" latex.....	1504
(1) Medium solids.....	1504
(2) High solids.....	1504
2. Applications.....	1505
3. Nomenclature.....	1505
B. Butadiene-acrylonitrile (NBR) latexes.....	1506
C. Neoprene or polychloroprene latexes.....	1506
D. Miscellaneous including some new types.....	1507
1. Vinyl pyridine latex.....	1507
2. Butyl latex.....	1507
III. Product trends.....	1508
IV. Process trends (Manufacture).....	1509
A. Latexes from emulsion polymerization.....	1509
1. Hot latexes (SBR type).....	1509
2. Cold latexes (SBR type).....	1509
a. Methods of making.....	1510
b. Equipment.....	1513
B. Manufacture of latexes from solid rubber.....	1514
V. Evaluation and fundamental studies.....	1514
A. Latex viscosity.....	1514
B. Electrolyte effect in latexes.....	1515
C. Stability and mechanism of formation of cream.....	1516
D. Seeding for uniform particle size.....	1517
E. Particle size measurement.....	1517
F. Particle aggregation.....	1518
G. Film formation.....	1518
H. Filler reinforcement.....	1518
I. Aging resistance of articles formed from latex.....	1519
VI. Conclusion.....	1519
VII. Acknowledgment.....	1519
VIII. References.....	1519

I. INTRODUCTION

Natural rubber in latex form had attained a relatively small but well-established use prior to any serious attempts to commercialize synthetic rubber. A comparison of the actual and proposed applications of natural rubber latex in 1936¹ with those of present-day synthetics shows that practically all of the present major uses were recognized at that time, although the variety of polymer types available has made the synthetics much more satisfactory for some of them than natural rubber could ever be. It is a rather remarkable coincidence that the polymerization system which was found to be most convenient for the manufacture of a variety of types of synthetic rubber resulted in a latex very similar to the natural product in many respects. As a result, the development of latex uses for synthetic rubbers proceeded almost without interruption as the polymers themselves were developed.

TABLE I
LATEX CONSUMPTION IN THE UNITED STATES, LONG TONS—DRY WEIGHT

	Natural latex	% of total natural rubber	SBR latex	% of total SBR	Poly-chloroprene latex	% of total neoprene rubber	NBR latex	% of total NBR
1943	9,578		15					
1944	6,085		6,598					
1945	3,886		15,197		7,077			
1946	5,724		24,810		13,603			
1947	13,909		22,474		6,087			
1948	28,489		23,441		4,500			
1949	36,117		21,500		3,750			
1950	56,138		23,680		2,530			
1951	46,750		31,031		6,279		2,628	
1952	53,567		40,562		7,368		3,093	
1953	67,375		46,473		7,981		3,654	
1954	75,931	12.7	44,173	8.8	7,251	12.7	4,507	25.4
1955	86,478	13.6	63,982	8.6	8,736	12.0	8,495	32.6
1956	73,100	13.0	65,380	9.0	8,733	11.7	8,934	34.4
1957	75,009	13.9	68,305	8.9	9,539	12.6	10,230	37.6
1958	70,183	14.5	60,283	8.2	9,555	13.7	10,549	39.7
1959	71,745	12.9	83,146	9.4	11,894	13.8	12,458	36.8
1960	49,998	10.4	86,757	9.6	11,222	13.8	12,954	40.3
Average		13.0		8.9		12.9		35.3

The major types of rubbery diene polymers and copolymers available commercially as latex from emulsion polymerization systems are: butadiene-styrene rubber, butadiene-acrylonitrile rubber, and neoprene.

However, there are also a number of variations of these polymers such as those where a third monomer has been added in manufacture in order to give a product to perform some special function. The most important of these are products containing either a basic or an acidic monomer.

A dispersion, which is termed a latex, as made from solid butyl rubber is also available commercially.

The present active development of new polymerization methods in which synthetic rubbers with improved properties are made in nonaqueous systems presents both problems and opportunities to the latex manufacturers. As the polymer manufactured for use in solid form does not go through an in-process latex step, it is evident that the development of latexes or dispersions for use

as such will require considerably more effort than was the case in the emulsion polymers. This situation is alleviated somewhat by the fact that many of these polymers are made in solutions which can perhaps be emulsified and stripped of solvent without too greatly complicating the process; although production techniques will never be as close to those for solid polymer as in the case of emulsion polymers. At present these artificial dispersions are not available in as small particle sizes or as low emulsifier coverage as are latexes from emulsion polymers. This will be discussed further under the section on "Process Trends".

The butyl latex referred to above is evidence that such products will be developed as the need arises. It will undoubtedly be joined by similar latexes from butyl modifications and other solid elastomers as uses develop.

There is another large class of latex products in which the polymers are essentially plastic rather than rubbery. These include styrene-butadiene polymers high in styrene, polyacrylates, polyvinyl acetate, polyvinyl chloride, and polyvinylidene chloride. These products are considered to be outside of the scope of this review.

The consumption² of the major types of synthetic latexes and of natural rubber latex in comparison with total rubber consumption of the corresponding types is summarized in Table I. In general, the percentage of polymer in latex to total polymer of a given type has been fairly stable. It is interesting to note that over the last few years both polychloroprene and natural rubber latex held to just about 13 per cent of corresponding total elastomer usage, although the absolute volume of polychloroprene has increased while that of natural rubber has decreased. In 1960 natural latex usage dropped sharply. This resulted largely from two forces: (a) the increasing competition from urethane foam, and (b) higher percentage of SBR in foam latex sponge compounds. SBR latex use accounts for a somewhat smaller percentage of total polymer, averaging very close to 9 per cent over the last several years. However, there appears to have been a slow gain in the last couple of years. Nitrile latex is by far the most important relative to the dry polymer with consumption averaging about 35 per cent of the total, and approaching 40 per cent in some years. Total overall latex consumption has been close to 11 per cent of overall elastomer usage during the past decade.

II. LATEX TYPES

A very large number of types of synthetic rubber latexes are available. A comprehensive listing including manufacturers, typical properties, and some suggested applications has recently been published³. A classification into nine major types was made by Bolam⁴. Price lists which include most available products but no properties other than general types are published regularly by the rubber trade journals^{5, 6}.

A. SBR AND RELATED LATEXES

Manufacture of SBR latexes was started in the Government GR-S program early in World War II. This general category represents by far the largest volume of production. Developments up through 1953 have been reviewed by Howland⁷. A number of monographs^{8, 9, 10} on applications of latex which have appeared in the past ten years have contained chapters devoted to synthetic latexes, and also extensive information on their use. Bibliographies are

also provided in some cases^{7, 8}. In addition, a brief general summary of the field with some references up through 1958 was published in a new book, "*Rubber Technology*"¹¹.

1. Types

The SBR latexes may be divided into the "hot" and "cold" types and subdivided into low and medium solids and high solids.

a. "Hot" Latex

Those that are in the true elastomer field are mainly medium solids, and many of those now produced are the same as were developed under the Government program or somewhat higher solids modifications of these although some have been varied slightly to improve such properties as freedom from cream and microcoagulum, general stability, and better color and aging resistance in finished articles.

Many of the high (60 per cent) solids types have disappeared, although two still remain but in less volume than previously. These are the 2003 (butadiene-styrene) and 2004 (polybutadiene) types.

Further mention of "hot" types will appear in other parts of this manuscript.

b. "Cold" Latex

(1) *Low and medium solids.*—There has not been as great a demand for medium solids "cold" latexes as for the "hot" variety. However, there have been several new products in the field of medium solids latexes (around 55 per cent solids) some of which have been made by agglomeration processes. Also, some high productivity 40 to 45 per cent solids latexes have been developed for use in agglomeration procedures for making high solids latexes for foam sponge. In some cases these may not have been sold as such because of lack of demand.

(2) *High solids.*—The real interest in this field lies in foamed latex sponge. For this application a latex of at least 60 per cent minimum solids is required.

Around 1953 there was a number of high solids latexes⁷ among which were X-753 and X-758. The latter was made in the new sodium formaldehyde sulfoxylate activated recipe, which will be mentioned under "Process Trends"; and X-753 was from 87/13 butadiene/styrene, while the X-758 was a 70/30 butadiene/styrene variety. The X-758 became SBR Latex 2105 which is the principal one of the original type direct high solids foam sponge latexes remaining from the original group. However, SBR Latex 2107 which is the same as 2105 except using a 50/50 butadiene/styrene ratio is still being made; but it is not used for sponge. The use of 2105 grew to very large volume, and it was employed in most of the foam sponge manufactured for a number of years and is still being used in large quantity.

A great amount of research effort has been put into making better and/or lower cost foam sponge latexes, and this has been stimulated by the competition of polyurethan foam.

Most of the procedures followed have involved agglomeration techniques which are discussed in a subsequent section. This has resulted in new commercial latexes by such techniques as the freeze process and the chemically promoted agglomeration.

Some of these new latexes offer the advantage of lower nonrubber content and higher solids (some as high as 68 per cent minimum).

Whereas some companies could make foam sponge on a 100 per cent basis or an 80/20 SBR/natural rubber basis from SBR Latex 2105, others could not. Much research therefore has been conducted for latexes that would more universally give outstanding foam properties when used on a 100 per cent or an 80/20 basis. Also, because of the economic battle with polyurethan foam, the effort has been to find latexes that would give lower cost foam.

The effort continues strongly in this field with the main effort on getting a product or means that will give a normal modulus foam with far less rubber than used at present.

2. Applications

Some of the SBR latexes like any of the solid polymers may be called general purpose products; but in the main, SBR latexes are special purpose products. In the case of natural latex, compounding techniques were developed in an effort to make it suitable for many applications. However, in the case of synthetics, in addition to compounding development, the latexes and the contained polymers are designed or tailored to give optimum results for many individual uses. This, of course, gives application opportunities not available when only natural latex was in existence.

The major uses have been described elsewhere^{7, 8, 9}. A more recent article describes the use of a number of elastomers as beater additives in paper manufacture¹². The most publicized recent change in the use pattern has been the decrease in latex foam production caused by the growth of polyurethan foam. In spite of the recognized deficiencies of the latter, and the development of improved foam latexes (see below), the economics of urethan foam manufacture have enabled it to capture a considerable share of the market. These relationships have been discussed¹³. Because of the higher average price of natural latex, and the problems involved in switching back and forth between natural and synthetic, a large part of the volume decrease has been at the expense of the natural product.

The major growth area for the SBR latexes has been in the textile field, particularly in the carpet industry. The popularity of foam backing on carpet has provided a considerable outlet for the types of latex displaced from seating foam, and the use of latex as backsizing on other types of carpet continues to grow. However, only part of this growth has been in the rubber latexes; a considerable fraction comprising the noncuring backings has been in the field of more plastic types.

Some very interesting effects have been obtained by frothing latex in or on a fibrous substrate. A method for simultaneously frothing and gelling soap emulsified latexes has been described in the patent literature¹⁴.

The application of frothed latex directly to the back of carpets, gelling, and vulcanizing appears to be a growing field.

3. Nomenclature

Under the Government Synthetic Rubber program, a four-digit numbering system was set up in which the first two numbers designated the polymerization temperature; and the last two numbers were assigned serially as new products were developed. Two series of numbers were used for latex products: The 2000 series for "hot" latexes, and the 2100 series for "cold". A relatively small number of products were available, and each of them might be produced at any

one of several plants. In the period immediately following the purchase of the GR-S plants by private companies in April, 1955, the major producers continued to manufacture latexes under the former designation, adding their own trade names (e.g., 2105 latex became NAUGATEX 2105, Pliolite 2105, FR-S 2105, etc.). This practice has continued to the present time, and the bulk of SBR latex manufactured is probably still in types bearing Government designations.

The ASTM proposed that this GR-S nomenclature system be continued with numbers in each series to be assigned serially. Descriptions of the latexes were to be published in the trade journals. A few latex designations were issued under this plan¹⁵, but most producers appear to prefer to apply numbering systems of their own. As a result, a large number of new products are now appearing with a variety of designations. This trend appears to be continuing.

B. BUTADIENE-ACRYLONITRILE LATEXES

The nitrile latexes are generally classed as special purpose products although they are used in a rather wide variety of applications. Their use seems to depend more on the polarity and thermoplasticity of the polymer than on the oil resistance which is the outstanding property of the solid polymer, although the latter is a factor in some applications. In major uses such as paper saturation and as adhesives, small particle size is desirable for good penetration and rapid setup on drying. As a result, the largest volume products have been medium (45-55 per cent) solids latexes emulsified primarily with carboxylic acid soaps.

Films deposited from nitrile latexes may be vulcanized with sulfur and ultra-accelerators, but for most uses the polymer is used in the unvulcanized form.

These latexes have been used with a mixture of urea and melamine-formaldehyde to improve the finish of cotton and other fabrics¹⁶.

A recent development in the nitrile latex technology has been its use in oil-resistant foams for lubricators in heavy-duty bearings such as railroad car journal boxes. Special high solids latexes polymerized at low temperatures have been developed for this application. Also one has been reported that has been made by freeze agglomerating¹⁷ a medium solids butadiene-acrylonitrile latex. These products are quite similar in handling properties to the SBR foam latexes and are processed by essentially the same technology. A brief description of compounding techniques has been published recently¹⁸. This nitrile type foam sponge, besides having resistance to oil and dry cleaning fluids, can be made to have practically no odor. It is better than foam from many other latexes in respect to this property.

C. POLYCHLOROPRENE LATEXES

The polychloroprene latexes are the oldest of the commercial synthetic products, having been introduced in the early 1930's. Like the nitriles, they are considered to be special-purpose latexes. Important properties include high gum tensile, oil and solvent resistance, good aging properties, and flame resistance.

A brief review of polychloroprene latexes was published in 1954¹⁹. Since that time a number of new latexes have been introduced, and a number of papers have been published on new studies and on applications. Another general article²⁰ appeared in 1957 which discusses available types up to that time including new ones introduced since 1953, compounding, and applications.

The main applications of the neoprene latexes are in bonded fibers, latex foam, adhesives, coated fabrics, protective coatings, paper, elasticized concrete, and dipped goods.

Bulletins have been issued by the du Pont Company concerning applications as follows:

1. Neoprene Latex Foam (BL-335).
2. Oil Resistance of Neoprene Latex Compounds (BL-352).
3. Saran as a Cure Activator for Neoprene Latex Compounds (BL-359).
4. Neoprene Latex Adhesives (54-3).
5. Progress in Neoprene Latex Adhesives (WAGF June 1960).

A rather new use that developed for neoprene latex during recent years was the use in making a foam to replace cotton waste in railway car journal boxes. The neoprene foam was used because of its oil resistance and because it would withstand the temperatures involved.

The amount of neoprene latex used per year has been shown in Table I. As noted there has been a steady increase in usage except for 1960. Here, the consumption was very close to that of 1959 where an increase might have been expected. This was undoubtedly due to the general drop in a number of business lines during 1960. Actually, total latex consumption (all types) for 1960 was about 91 per cent of the 1959 sales.

D. MISCELLANEOUS INCLUDING SOME NEW TYPES

1. Vinyl pyridine latex

The vinyl pyridine latexes were developed specifically for use in adhering rubber stocks to fibers, particularly nylon²¹. Their major use is as saturants for tire cords. In general the polymers are high diene types containing 10-15 per cent copolymerized 2-vinyl pyridine and an approximately equal amount of styrene. The latexes are emulsified largely with anionic soaps and are of about 40 per cent solids content.

Some of these latexes contain chemical additives which make them resistant to coagulation on freezing and thawing as might occur in the wintertime when material is left outside too long and then brought into the plant for use.

2. Butyl latex

Recently work has been done to make latexes from solid rubbers, comparable to known rubber and polymer latexes prepared by emulsion polymerization.

A recently publicized latex made directly from polymer is butyl latex. Some typical properties of the first commercial example and some uses, properties, and other information have been published²² and are discussed below.

Properties	
Color	White
Total solids, weight %	54-55
Specific gravity at 70° F	0.96
Density, lbs./gallon	8.1
pH	5-6
Particle size, microns average	0.5
Range of 95%	0.05-1.0
Surface tension at 70° F dynes/cm	30-38
Anionic emulsifier (% on latex)	2.5

In general these new latexes from solid rubber and polymers differ from previous dispersions from solid polymeric material by older methods in that they can be made in smaller particle sizes. Also, they can be made more readily with the same type emulsifiers occurring in emulsion polymerized systems, although the surface coverage is normally considerably higher.

The higher emulsifier stabilization requirements in the preparative processing of a latex prepared as an after treatment of an already formed polymer leads to finished latexes of unusual stability to shear and to polyvalent ions. This greatly broadens the horizons of the use of latex rubber.

Butyl latex can be compounded with curatives used for other latexes and then vulcanized, although more drastic conditions are required, to commercial articles. Many of the techniques of application are similar to or modifications of those employed with previously known latexes.

Vulcanizates of products from butyl latex have good resistance to aging, weathering, ozone, and chemicals, and low permeability to moisture and gases.

It is understood that butyl latex was originally developed for use in cord dips in building butyl rubber tires. However, the properties are such that it may be useful in other fields of application such as paper and textile coatings, laminated barrier papers, nonwoven fabrics, as well as many others²².

III. PRODUCT TRENDS

Under the Government program, SBR latexes were classified as "hot" or "cold" depending on whether they were manufactured at temperatures of 120–150° F or at 40–50° F. In general this classification has been continued, although there has probably been some broadening of the ranges. Although products are or have been available in both types over a broad spectrum of monomer ratios, there has been a marked trend toward concentration on the higher styrene (40–50 per cent bound styrene) polymers in the "hot" latexes, and lower styrene (mostly 20–30 per cent bound styrene) types in the "cold" latexes. This is a logical development in view of the much greater improvement in properties of the high diene polymers with reduction in temperature of polymerization. For most uses where the large volume, higher styrene latexes of the 2000, 2001, and 2002 type are used, high temperature polymerization appears quite adequate; and little advantage is found for the "cold" polymers. An exception to this generality exists where coatings with high filler loadings are used, particularly for curing type carpet backings. Here an advantage can be shown for the "cold" polymers in retention of physical properties at the high filler loadings. This characteristic is reflected in the continued use of 2107 (50/50 butadiene/styrene) latex in these applications, and the development of similar but more economical, lower solids types such as NAUGATEX 2113. Polybutadiene latex is available in both "hot" and "cold" types. It is used to improve the structure of latex foam, and for some miscellaneous applications.

The most striking recent advances in SBR latexes have been in the "cold", high diene, high solids types. These are primarily designed for the manufacture of foam sponge, although they are also used in other applications where high polymer quality and high solids content are important. During the latter part of the Government Program, an intensive development effort was carried out on this type of product which culminated in the production of 2105 latex. For several years prior to and after sale of the synthetic plants, this latex, produced by several manufacturers, was the standard synthetic foam latex.

Recently, however, a number of new latexes have been commercialized. Improved product characteristics—primarily for latex foam—have been in the direction of higher solids content and faster gelation with sodium silico fluoride. Two of the new products are being supplied at solids content in excess of 68 per cent (NAUGATEX J-8174, Pliolite 5352, FRS-200).

There has also been a tendency toward higher solids contents in the "hot" SBR latexes without any cost premium. A number of products are now available at the price of 2000 latex but at solids contents close to the 50 per cent level, representing a 6-8 per cent increase.

The incorporation of monomers containing functional groups has led to the development of several new commercial products in recent years. Functional groups, of which carboxylic acids are most commonly used, confer compatibility and possibly some degree of chemical bonding with polar substrates on which the nitrile latexes are most frequently used. Since neutralization of an acid-containing polymer will give a "built-in" emulsifier, these monomers allow the preparation of stable "emulsifier-free" latexes^{23, 24}. Such products have been available experimentally for a number of years, but do not appear to have attained commercial acceptance.

IV. PROCESS TRENDS (MANUFACTURE)

A considerable amount of work has been done recently on the improvement in manufacture, including new methods of making synthetic rubber latexes. This covers all types of products based on various elastomers such as "hot" and "cold" latexes and those from various solid rubbers.

A. LATEXES FROM EMULSION POLYMERIZATION

In this field the greatest attention has been paid to medium solids and high solids latexes.

1. "Hot" latexes (SBR type)

Most of the latexes in this class are under 60 per cent solids, and there has been very little demand for 60+ per cent solids. In fact, with the exception of the 2003 (butadiene/styrene copolymer) and 2004 (polybutadiene) types employed mainly in connection with high impact plastics, most of the previous very high solids latexes have practically disappeared from the market since they were used in general for foam sponge; and the "hot" foam sponge latexes have been very largely replaced by "cold" latexes for this application. In general the very high solids latexes are more costly than those of lower solids; and since polymer properties are sufficiently good, the economic angle has determined the use of the medium solids products.

Most of the medium solids (45 to 55 per cent) "hot" latexes are made by direct polymerization with or without heat concentration. Some previous types made in 1954 are now made at higher solids. This has been accomplished by techniques to give a somewhat larger average particle size than was present in the earlier parent latexes. Since the techniques employed for this are also used for high solids "cold" latexes, they will be discussed below.

2. "Cold" latexes (SBR type)

Published process and equipment improvements have been largely associated with improvements in this field.

a. Methods of Making

A new activator system²⁵ which allows better process control and lighter latex color was introduced and generally accepted near the end of the Government Program. The major improvement, however, has been the development of systems which allow much faster polymerization rates with concurrent improved product characteristics.

In standard emulsion polymerization of fast producing low or medium solids SBR and related latex recipes, the average particle size is too small to concentrate the latex to more than 40 or 45 per cent solids without the latex becoming too viscous⁷. In fact in all standard emulsion polymerization of SBR type materials, the particles start small and build up in size during polymerization as the system adjusts to the amount of available emulsifier.

TABLE II
METHODS OF INCREASING LATEX PARTICLE SIZE

- I. In situ (during polymerization) methods
 - A. Hydrocarbon-water ratio adjustment
 - B. Type and amount of emulsifier system modification and method of using
 - C. Seeding
- II. Solvent addition (for either phase)
- III. Methods involving partial soap neutralization or pH drop
 - A. Nonvolatile emulsifier techniques
 - B. Volatile base emulsifier or electrolyte
- IV. Electrolyte addition
 - A. Nonvolatile
 - B. Volatile
- V. Temperature manipulation
 - A. Freezing
- VI. Chemical promoter addition
- VII. Other methods
 - A. Combinations of the above

One of the difficulties with the present direct high solids latexes is the long reaction times which are one of the factors causing low productivity as compared to standard solid SBR rubber manufacture. In order to increase the productivity and consequently reduce the cost of manufacture, considerable work has been conducted in recent years on low cost procedures for increasing the particle size of fast producing systems so that they can be heat concentrated to low viscosity 60+ per cent solids. The effort to get low cost has increased even more in the last two or three years due to the competition of lower price polyurethan foam sponge which has been cutting into the sales of foamed rubber latex sponge, the largest use for 60+ per cent solids synthetic rubber latexes.

In general, the methods of increasing particle size are listed in Table II.

Some methods described previously⁷ which fall under some of the above headings are not discussed here, but, the more important recent developments are reviewed.

The hydrocarbon-low water recipes (I A)⁷ were used for many years, and some are still in use for making high solids latexes. These also usually involve increment addition of some ingredients such as emulsifier and electrolyte.

Concerning I B, some of the recipes have been built on low soap along with other features such as low water⁷ as well as increment addition of soap. Also some emulsifiers such as dimer acids have a specific effect of causing a greater-than-normal growth of average latex particle size^{26, 27} and can be used to make direct high solids latexes at a rather rapid rate. Some of these have been made to almost 100 per cent conversion where usual latexes are made to 60 to 80 per cent conversion. Also some of these do not require concentration.

By adding seed (previously polymerized) to batch or continuous process SBR polymerization, latexes can be produced with larger-than-average particle diameter^{7, 28}, the size depending on the amount and particle size of seed and the nature of the recipe and polymerization technique. Latexes of 68+ per cent solids can be attained by this technique. In continuous process using twelve or more reactors in a line, seeding can be obtained by recirculating a portion of the latex which may be added at any desired reactor.

The main disadvantage of the procedures under I above is low productivity.

The solvent agglomeration (Method II in Table II) as mentioned may be accomplished by treating finished latexes with suitable solvents for either the hydrocarbon^{29, 30} or the water phase³¹. Concerning the case of the former, when a small particle size latex is agitated with the proper amount of solvents such as styrene or benzene and these are then removed by evaporation under vacuum, a latex of increased particle size is obtained which can be concentrated to over 60 per cent solids. Actually, some solvent agglomeration takes place in ordinary emulsion polymerization, where the unreacted monomers act as the solvent. The latter is "in situ" agglomeration (see I A).

Concerning solvents for the aqueous phase, materials such as acetone added to the latex in suitable quantity increased the particle size. The acetone subsequently may be distilled off and the latex concentrated by creaming or evaporation.

In III A, an alkaline latex may be partially neutralized with an acid or a material that forms a strong acid, and subsequently the average particle size will be increased^{32, 33, 34, 35}. This can be done most satisfactorily when the latex contains a sulfonate emulsifier in addition to soap emulsifier. The pH may drop to 5 or 6. After coalescence of particles, the pH is again increased with fixed base; and then the latex may be heat concentrated. Also, in another method of pH of a latex may be decreased with a volatile acid as carbon dioxide, then the pH raised with ammonia, and the ammonium carbonate formed removed by steam stripping during the concentrating step.

The III B case differs in that part of the emulsifier system may be a volatile base soap such as ammonium oleate. When the latex is being stripped of unreacted monomers, ammonia is lost thus decreasing the soap in the system. In adjusting to the lesser soap, the average particle size increases by coalescence of particles. The pH is then increased with fixed base and the product heat concentrated. This may also be accomplished by adding volatile base electrolyte as ammonium chloride to a finished fixed base soap latex³⁶. This is then steam stripped of ammonia; and after an increase in particle size is accomplished, fixed alkali is added; and the latex is concentrated.

In connection with IV A, high nonvolatile electrolyte (up to 5 parts or more per 100 parts of polymer) added to low or medium solids SBR or related latex

increases the particle size^{37, 38, 39} so the latex can be concentrated to high solids. One disadvantage of this technique is the large amount of nonrubber material left in the latex.

Similar amounts of volatile electrolyte such as ammonium bicarbonate⁴⁰ when added to latex cause coalescence of particles and so increase the average particle size. After this the electrolyte can be removed from the latex during heat concentration of the latex. However, this method has the disadvantage that the electrolyte would have to be recovered in order to obtain maximum economy from the method.

In general, electrolytes in smaller quantities play a part in aiding agglomeration in many other procedures of obtaining particle size increase in synthetic rubber latexes.

Concerning the manipulation of temperature (V A), an important development was the finding that freezing of certain latexes caused an increase in particle size^{41, 42, 43}. The latexes when thawed out are concentrated to high solids. In one of these procedures, a medium solids latex that is stable to freezing, is quickly frozen on a rotating freeze drum, is removed in chips to a tank and quickly thawed, and then is heat concentrated. One advantage of this method is the ability to make high solids content latexes with low nonrubber solids. One disadvantage of the procedure is a rather high capital investment.

A very interesting and unique discovery was that certain colloiddally active chemicals (VI) speed up agglomeration⁴⁴ by any of the other known methods of increasing particle size. Also, a very unique chemical has been developed that will cause coalescence of particles without the aid of any of the other procedures except that concentrating and crowding of the particles is beneficial to the process. In general, specific chemicals or classes of chemicals give the best results in given agglomerating techniques.

One of the unusually unique chemical promoters is polyvinyl methyl ether⁴⁴. The best results are obtained when the latex is heat concentrated to about 55 per cent solids where the latex becomes very viscous. It then thins out, and surface tension drops. As concentration continues, the solids rise to around 70 per cent. When a sample of polyvinyl methyl ether (PVM) that requires 0.25 parts per 100 of polymer for particle size increase is treated by certain procedures⁴⁵, its agglomerating effect is improved so that as little as .001 parts per 100 of polymer will give agglomeration under similar conditions to those used for the untreated material. Also, when using the proper amount of this treated material, no electrolyte appears to be required in the system to get suitable particle size increase. A commercial latex (NAUGATEX J-8174) is being made by the above improved PVM procedure^{44, 46}. This new procedure has the advantage of extreme simplicity. It differs from standard plant procedure only in that a trace of chemical is added just prior to the start of concentration.

Referring to VII above, two or more of the above procedures can be combined to give particle size increase. In these cases, less of any one treatment is necessary, since different types of treatment appear to be at least additive. Certain combinations have already been indicated in the above discussion of various agglomeration methods.

Actually in making high solids latex by the so-called direct polymerization procedure, the large particle size formation during polymerization (in situ) is aided by a combination of agglomeration factors such as (1) solvent (monomer) agglomeration as mentioned previously, (2) electrolytes, (3) low water to

monomers, (4) low emulsifier to monomers at the start. None of these effects alone in the amount used during polymerization can give a satisfactory amount agglomeration. For instance, the electrolyte is employed in an amount that by itself would have practically no agglomeration effect if added to a low electrolyte finished latex. In this case it is impractical to use more in the polymerization recipe because it would kill polymerization.

It should be mentioned that many more agglomeration systems have been found than those listed here. Some are quite good while many others have failed to gain importance because of extensive macroagglomeration (coagulum formation). The unique systems are those that operate with essentially no loss of material as coagulum, have simplicity, and give very low cost operation.

b. Equipment

Previously⁷, in heat concentrating, one type of heat exchanger was mentioned. Since that time a tall vessel for concentrating latex under vacuum has been developed that may be used with any type of shell and tube heat exchanger. The heating of the exchanger may be either by direct steam or hot water.

Also for some latexes with the proper stability, concentration is conducted with a turbulent film evaporator⁴⁶. This is the type of equipment that has been used for evaporating fruit juices and milk. Some small modifications of the equipment were devised in order to make the equipment satisfactory for latex concentration.

In addition to the above, a continuous system for concentrating latex has been developed⁴⁷ in which the equipment contained a columnar vessel 45 feet high by 9 feet in diameter. The latex occupied the bottom 15 feet of the column. The column was connected with a pump and heat exchanger to circulate the latex from the bottom of the vessel back into it at an opening about 30 feet up the column. Evacuation of the concentrating column was accomplished by a single stage jet discharged to a surface condenser and thence to a Nash Hytor vacuum pump.

Fresh latex was continuously blended into the recirculation stream, and a portion of the latex from the bottom was continuously removed with a flow controller at 60+ per cent solids while the remainder was continued in the recirculating system. It is reported that this procedure has advantages over the batch concentration process such as less entrainment losses, less foam overs, less operator supervision, less down time, easier control of solids, and more uniformity.

In the beginning of the Government Program, all SBR latex production was by the batch process; and large quantities are still made in this manner. However, in recent years, where large volume production of certain high solids latexes such as SBR 2105 latex has been required, the polymerization has been made by a continuous process using twelve to sixteen reactors in a line. This can be advantageous because it utilizes the complete reactor space thus increasing productivity and also offering the opportunity to add ingredients incrementally or even new ingredients at the proper stage of polymerization as well as offering a chance to modify the mechanical treatment of the latex during the course of polymerization.

In the batch process of latex production, the usual size of reactors was originally of 2,000- to 3,750-gallon capacity. However, more recently some operators have utilized reactors up to 10,000-gallon capacity with excellent success.

The tendency of latex to deposit polymer on surfaces in contact with it makes measurement of flow rates a continuing problem. An electromagnetic flow meter which alleviates this difficulty to some extent has been developed⁴⁸.

B. MANUFACTURE OF LATEXES FROM SOLID RUBBERS

A method that has been used recently to make latexes from solid polymers such as butyl rubber is the solvent method. In this procedure a solution of a rubber or a related polymer, in a water insoluble organic solvent, is emulsified in an aqueous medium using known emulsifying agents and then distilling the solvent from the "new latex" thus leaving the rubber or polymer in the form of small particles^{49 to 57}. Also chlorinated polymer latexes have been produced by the solvent technique^{58, 59}.

Also, it has come to the authors' attention that latexes have been made from *cis* polyisoprene (synthetic natural rubber), ethylene/propylene copolymer rubber, and other materials by a solvent method similar to those referred to here.

V. EVALUATION AND FUNDAMENTAL STUDIES

A. LATEX VISCOSITY

The viscosity of latexes, particularly at high solids content, has been a subject of continuing study⁶⁰. Maron and co-workers at Case Institute have published a series of papers on the rheology of a variety of latexes⁶¹. The effect of particle size and distribution on the per cent solids that can be attained in a dispersion or a latex and still have a handleable product has been reported by several authors^{61, 62}. The early work indicates that when a blend of small and large particles are used, that optimum solids are obtained when 65 to 74 per cent of the polymer is in the large particles. More recent studies^{63, 64} have used various mixtures of latexes from three products having different particle sizes. The work confirms that obtaining a desirable viscosity on concentrating to high solids, depends on (1) large particle size, and (2) particle size distribution with best results being obtained with the widest differences in particle size and that best results occur with 75 per cent of the polymer being in large particles.

A mathematical study was made related to the above, and it was shown that starting with latexes and blends of known particle sizes, the solids to be expected for a given viscosity could be calculated. The investigation involving spacing showed that an approximation to the viscosity versus concentration relation could be made from the mean particle spacing, using only one arbitrary constant. The packing constant for monodisperse latexes could be evaluated from the volume concentration of polymer at which the viscosity increased beyond measure (about 74 per cent for uniform particle size latex). The study covered both latexes of one particle size and those of a blend of two particle sizes. With the latter by use of the packing constant obtained from limiting concentration and one arbitrary constant, a satisfactory fit between the viscosity-concentration curves obtained experimentally and those deduced from particle spacing data was achieved.

A study⁶⁵ has also been made of factors that influence viscosity of butyl latex. This work shows that viscosity can be increased or decreased by appropriate addition of inorganic salts, amine salts, acids, or by ion exchange treatment. The change in viscosity is presumably due to controlled micellation or insolubilization of the dissolved, unadsorbed emulsifier.

The flow behavior of Neoprene Type 60 latex has been studied⁶² in order to see if the disperse phase has any effect on the rheology of this latex as compared to that of other latexes such as SBR latexes. The variables investigated were shear stress from 30–800 dynes/cm² at concentrations of 0 to 60 per cent solids, at a constant temperature of 29.94° C.

It was shown in this research, that below 0.20 volume fraction that the latex was Newtonian; and above this, it was non-Newtonian. An equation was developed showing the relation of relative viscosity to concentration and stress which held at all concentrations investigated. With the latex used for the study, the viscosity goes to infinity between 0.55–0.61 volume fraction; and since this takes place at a lower volume fraction than with SBR latexes, it indicates cubical rather than tetragonal or rhombohedral close packing. Another respect in which the flow behavior differs from SBR latex is that no maxima has been observed in the curves down to a stress of 30 dynes/cm².

B. ELECTROLYTE EFFECT IN LATEXES

Some work has been done on electrolytes in latex other than that mentioned earlier under agglomeration in sections IV A 1 a and V A and mentioned later under V C. This is discussed below.

If a latex is made without electrolyte as reported by Fryling and Gindler⁶⁶, a gelled mass is obtained with a consistency like petrolatum. However, if a small amount of electrolyte is added to this finished product, it thins out to a free-flowing latex. Also, if the same amount of electrolyte is used in the polymerization recipe, a fluid latex results. It is explained that the latex particles are surrounded by ion pairs and that because the particles have either no charge or a very weak negative charge, there is no repulsion. Hydrogen bonds are then formed through a three-dimensional or "gel" system. The water layer keeps the particles from coalescing. It is proposed that electrolytes added to the system break the hydrogen bonded ligands from the aqueous sheath thus permitting free movement of the particles. The authors suggest that a good problem would be determining the thickness of the absorbed water layer of electrolyte-free latex gels. Other studies such as those on agglomeration indicate that the electrolyte affects the thickness of an absorbed aqueous layer on the particles and that the layer gets smaller as the electrolyte is increased.

Another study²⁶ shows the effect of the amount of electrolyte in a low water recipe on minimizing the amount of floc formed during polymerization and finishing of a latex. This investigation showed that the amount of floc decreased with increasing amounts of electrolyte and that the amount necessary for minimum floc formation increased as the amount of water to hydrocarbon increased in the recipe. The increased electrolyte functions to a large degree by causing an increase in average particle size thus bringing about a more stable latex. Because of this effect, the polymerization rate in many recipes is slowed down since the number of places for free radicals to start new polymerization has decreased. Thus a limiting factor in the use of electrolyte in latex polymerization is determined by its detrimental effect on polymerization rate. Frequently, the amount selected is a compromise that gives the best all-round economics. Another limiting factor on nonvolatile electrolyte in latexes for certain applications, is the amount of nonrubber solids added to the final latex.

C. STABILITY AND MECHANISM OF FORMATION OF CREAM

Stability of latexes is a problem still demanding much attention since difficulty is experienced with this property in both manufacture and application of latexes.

An article⁶⁷ on the effect of aliphatic detergents on the mechanical stability of polystyrene latex has some interesting information that may be helpful in understanding stability phenomena in elastomer latexes. In this research, the emulsifiers studied were potassium palmitate and potassium laurate; and also some work was included using a nonionic detergent of the polyethylene oxide class with and without soap. The mechanical stability data of ionic detergent systems are influenced very much by the nature and surface concentration of the adsorbed ionic detergent, and it appears that the stability may be largely due to steric interference of the adsorbed carbon chains. The surface concentration of adsorbed soap does not influence the electrokinetic potential of the particles. The mechanical stability of the nonionic system is quite poor. In this case it seems that the interference of adsorbed hydrocarbon chains is not enough to give very much benefit to this property. During this study it was found that a latex, containing both soap and nonionic detergent, was more stable than a latex containing either one alone. It was concluded that in this system, stability is dependent upon some co-operation between electrical and steric factors.

In the early manufacture of "cold" SBR latex, a layer of cream sometimes formed on the surface which, when mixed, in the body of the latex, had a detrimental effect on some physical properties of finished articles, such as the lowering of the tensile strength. Also, the cream caused changes in latex concentration that was very annoying to consumers of latex. This phenomenon was studied in order to eliminate it. This involved mechanism study⁶⁸ which gave some very illuminating information.

In the direct high solids latex the cream began forming between 18 and 35 per cent conversion and continued to increase until the end of polymerization. The cream formation was influenced by the kind and amount of soap; for instance, a soap that initiates a small enough number of particles in relation to its stabilizing action minimizes cream formation. Also cream can be minimized or prevented by timely incremental addition of sufficient stabilizing soap.

The effect of increasing the water to hydrocarbon during polymerization or introducing crosslinking of the polymer, served to increase the size rather than the number of agglomerates.

The effect of electrolyte on cream and coagulum formation in certain direct high solids latex recipes has been reported²⁶ and is referred to in section V B. In the ferrous sulfide activated recipe, with the lower amounts of electrolyte, large amounts of coagulum formed while, with intermediate amounts, large amounts of cream formed which decreased with increasing electrolyte, and finally with larger amounts only minor amounts of cream and coagulum were formed.

Some latex stability work has been published⁶⁹ which involved factors that influence the stability of low solids latex of the type manufactured for conversion to solid rubber and which was particularly concerned with variables connected with manufacture. Although this work was not conducted on the type of latexes that are produced and sold in the latex state, some of the information may be pertinent to these latexes. The work suggests that the instability that leads to creaming involves two steps, one of which consists of reversible aggre-

gates of particles, and the second, coalescence of the aggregates into large individual particles. Concerning the effect of variables, it is stated that stability decreases as temperature increases, as polymer concentration increases, that it is influenced by particle size and particle distribution and that it is affected adversely by surface evaporation.

Concerning the concentration effect, a brief discussion of stability of very dilute latexes is presented in an article on "Electrokinetic Potentials of Latexes"⁷⁰. It states that latexes are stable on dilution if the pH is adjusted to that of the original latex. One reason given for stability on dilution is the decrease in probability of collision of particles which lead to coagulation. Another explanation involves particle absorption of hydroxyl and hydrogen ions which have specific activity in dilute systems and which can favor stability.

A conclusion in the article⁷⁰ in connection with electrokinetic potentials of synthetic latex mentions that there is no direct relation between degree of surface saturation by soap and the electrokinetic potential.

D. SEEDING FOR UNIFORM PARTICLE SIZE

The effect of seeding in producing uniform particle size latexes, primarily of interest for resin types, has been studied⁷¹.

It is reported that with polydisperse small size latex seed, that polydispersity decreases as polymerization proceeds, providing new particles are not initiated. It appears that growth of seed particles is somewhat greater in the smaller particles.

It is now known that if uniform particle seed is employed and no new particles are initiated in polymerization, that a latex can be obtained with quite uniform large particles of a desired size.

E. PARTICLE SIZE MEASUREMENT

The knotty problem of the measurement of particle size and particle size distribution has continued to receive attention. A counting device has been used to determine the distribution of particle size in butyl latex⁷².

This new method which is useful for particles in the region of 0.6μ to over 200μ , involves the flow of a suspension of particles in a conductive liquid through an aperture with simultaneous electric current flow. A series of electrical impulses occur each of which is proportional to the volume of the particle causing it. The count data and its treatment, resulting from the procedure, provide a particle size distribution. The only particle property that appears important in the determination is particle volume except in some special cases. The method is comparable with the best of the other methods except for a higher limit in the very small particle size range. The method appears very interesting particularly from the viewpoints of speed and simplicity.

An interesting method of determination of latex particle size distribution has been reported⁷³ which involves fractional creaming of latexes with varying amounts of sodium alginate. This is based on the fact that there is a relationship between the amount of alginate and the particle sizes accumulating in the cream. After the procedure has been calibrated against electron microscope results, particle distributions can be made very readily. The method employs well stabilized 10 per cent solids latex, and 50-gram portions of the 10 per cent solids latex are treated with varying amounts of alginate solution and sufficient water to make 200 grams of mixture; and creaming is conducted for 24 to 48

hours in separatory funnels. The cream solids are determined, and the data are employed for establishing the particle size distribution curve. This method is found to be especially good where there is a wide distribution of particle sizes.

Also, further work has been done on light scattering measurements for use in monodisperse systems⁷⁴. The procedure as developed gives the desired particle size information rather rapidly. One of the advantages over the electron microscope method is that the latter uses a dried sample which in some cases can cut down on the accuracy of the results due to such factors as particle agglomeration.

F. PARTICLE AGGREGATION

Work has been done on the particle aggregation of polyvinyl toluene latex by protein in the presence of various types and amounts of emulsifier and by Methocel in varying amounts⁷⁵. These studies give basic information that may prove to be applicable to the elastomers as well as the plastics field.

One very interesting point in this work occurred when Methocel was added to the system in varying amounts. With increasing small amounts, increasing aggregation occurred while, above a certain amount of Methocel, increasing amounts caused deaggregation or decreasing amounts of aggregation; and finally amounts were reached at which no aggregation occurred, and the thickener, Methocel, became a protective colloid.

G. FILM FORMATION

A study of the factors involved in film formation from polymer latexes⁷⁶ has given qualitative information on relationships of some system variables on particle coalescence to produce films. Features having influence are particle size, surface tension, rheological properties of the polymer, temperature, and rate of water evaporation. It appears that the most important factors are the capillary pressure resulting from the water surface in the interstitial capillary system and the resistance of the sphere to deformation. It appears that more knowledge of a number of factors will be necessary before film formation can be put on a quantitative basis.

H. FILLER REINFORCEMENT

In the first work on using carbon black latex film vulcanizates, products were obtained that gave tensile strength properties considerably inferior to vulcanizates from corresponding mill mixes.

In some later work^{77, 78} on butadiene/styrene copolymer latex, the effect of fillers including carbon black, on the strength of latex films was studied. This work showed fairly good reinforcement by carbon black.

In some recent work⁷⁹ a research study of variables has shown very good reinforcement of butadiene/styrene copolymer latex films with carbon black from latex mixes containing polymer, dispersed carbon black, and varying amounts of materials such as casein, gelatin, and alginic acid. The films have been made by drying and by electrolyte coagulation. The film vulcanizates from the latter method approach mill mixed vulcanizates of corresponding butadiene/styrene rubber and carbon black mixes in tensile strength.

This indicates that eventually latex researchers may be able to make a good tire tread by latex deposition.

I. AGING RESISTANCE OF ARTICLES FORMED FROM LATEX

It has been noticed that a few latex foam sponge articles have been returned to manufacturers in a relatively short time which have gone bad (partially resinsified) by an aging procedure that appears unusual. A study³⁰ has shown that this is promoted by nitrogen dioxide from combustion gases. This appears to be the first time that this phenomenon has been published. It raises the question as to whether this effect may not occasionally occur in service aging of other articles from unsaturated elastomers.

The nitrogen dioxide effect causes discoloration of finished articles, at least partly, by interaction with antioxidants to give colored bodies. This problem can be minimized by suitable compounding including selected antioxidants. The authors indicate that antioxidants or stabilizers better than existing ones, would be desirable to cope with this problem.

VI. CONCLUSION

Progress has proceeded at a good rate since the close of the Government Program in the spring of 1955. Improved latexes have been made, and the technology of manufacture and of application has advanced. Also progress has been made in fundamental latex research.

Some of the newer latexes representing the more important advances are those involving functional groups derived from the use of unsaturated monomers such as those containing amino groups and carboxy groups in the polymerization system, those from solid rubbers by the solvent emulsion technique, and those of higher solids content including the agglomerated latexes giving 68 per cent minimum solids at low viscosity.

Some of the applications of greatest growth are:

1. Carpet backing involving both sulfur curing and so-called self-curing (noncured) elastomer latexes. The latter obtain strength from polar groups including functional (carboxyl) groups and/or fairly high styrene content.
2. Foam sponge backed carpets.

In 1954⁷ it was suggested that synthetic rubber latexes would have a permanent place in our economy. This has now come to pass, and natural latex is decreasing in volume compared to total synthetic rubber latex consumption. It now appears that by forming a latex from *cis* polyisoprene (synthetic natural rubber) and adding it to our list of latexes, that our country could probably become independent of the natural product.

VII. ACKNOWLEDGMENT

The authors wish to thank the Naugatuck Chemical Division of the United States Rubber Company for permission to publish this review.

VIII. REFERENCES

- ¹ North, R. J., "Latex in Industry", First Edition, Rubber Age, New York, 1936.
- ² U. S. Department of Commerce (Industrial Reports).
- ³ *Rubber World* 143, 71 (1961).
- ⁴ Bolam, S. E., *Proc. Inst. Rubber Ind.* 4, 61 (1957).
- ⁵ *Rubber World* 143, 116, March, 1961.
- ⁶ *Rubber Age* 88, 1053, March, 1961.

- ⁷ Howland, L. H., in "Synthetic Rubber" edited by G. S. Whitby, J. Wiley & Sons, Inc., New York, 1954.
- ⁸ Noble, R. J., "Latex in Industry", Second Edition, Rubber Age, New York, 1953.
- ⁹ Cook, P. G., *Latex, Natural and Synthetic*, Reinhold Publishing Corporation, New York, 1956.
- ¹⁰ Stern, H. J., "Practical Latex Work", Third Edition, Black Friars Press Ltd., Leicester, 1955.
- ¹¹ Winspear, G. G. and Watermann, R. R., in "Introduction to Rubber Technology", edited by M. Morton, Reinhold Publishing Corporation, New York, 1959.
- ¹² Spector, H., *TAPPI* 41, No. 3, 116A (1958).
- ¹³ Rogers, T. H., *Rubber World* 132, 610-14, *ibid.* 733, *ibid.* 753-7 (1955).
- ¹⁴ Fairclough, J. T., U. S. Patent 2,858,282.
- ¹⁵ *Rubber World* 136, 718, August, 1957.
- ¹⁶ *Textile World* 104, No. 11, 135 (1954).
- ¹⁷ "Development and Application of a High Solids Nitrile Rubber Latex" by J. M. Mitchell, G. K. Watson, H. L. Williams, Polymer Corporation, Sarnia, Ontario, Canada. Presented at the Division of Rubber Chemistry, ACS Meeting in Louisville, Kentucky, April 20, 1961.
- ¹⁸ *Rubber Age* 78, 734 (1956).
- ¹⁹ Neal, A. M. and Mayo, L. R. in "Synthetic Rubber" edited by G. S. Whitby, J. Wiley & Sons, New York, 1954.
- ²⁰ Hartfield, E. P., *Rubber and Plastics Age*, 38, 970, November, 1957.
- ²¹ Borg, E. L., *Rubber World* 137, 723 (1958).
- ²² Miller, A. L. and Powers, K. W., *Rubber Age* 86, (October, 1959) Enjay Bulletin entitled "Enjay Butyl Latex 80-21".
- ²³ Eilbeck, G. E. and Urig, E. R., U. S. Patent 2,868,754, January 13, 1959.
- ²⁴ Miller, A. L. and Miller, V. A., U. S. Patent 2,880,189, March 31, 1959.
- ²⁵ Brown, R. W., Bawn, C. V., Hansen, E. B., and Howland, L. H., *Ind. Eng. Chem.* 46, 1073 (1954).
- ²⁶ Howland, L. H., Neklutin, V. C., Brown, R. W., and Werner, H. G., *Ind. Eng. Chem.* 44, 762-8, (1952).
- ²⁷ Miller, V. A. and Becker, R. G., U. S. Patent 2,876,203, March 3, 1959.
- ²⁸ Glasgow, G. U., Private Communication to ORR., October 5, 1945.
- ²⁹ Brown, R. W. and Howland, L. H., *Rubber World*, 471-477 (1955).
- ³⁰ Brown, R. W., U. S. Patent 2,897,168, July 28, 1959.
- ³¹ Rumbold, J. S., U. S. Patent 2,454,425, October 11, 1949.
- ³² Peaker, C. R., U. S. Patent 2,446,101, July 27, 1948.
- ³³ Svendsen, E. C., U. S. Patent 2,446,115, July 27, 1948.
- ³⁴ Rumbold, J. S., U. S. Patent 2,494,002, January 10, 1950.
- ³⁵ Willson, E. A., U. S. Patent 2,357,861, September 12, 1944.
- ³⁶ Howland, L. H. and Nisonoff, A., U. S. Patent 2,839,483, July 17, 1958.
- ³⁷ Peaker, C. R., U. S. Patent 2,393,261, January 22, 1946.
- ³⁸ Willson, E. A., U. S. Patent 2,444,689, July 6, 1948.
- ³⁹ Arundale, E., U. S. Patent 2,444,601, July 6, 1948.
- ⁴⁰ Rumbold, J. S., U. S. Patent 2,475,053, July 5, 1949.
- ⁴¹ Maron, S. H., Trumbull, D. and Elder, M. E., *J. Am. Chem. Soc.* 70, 586, (1948).
- ⁴² Talalay, L., Italian Patent 528,151 (British Patent 758,622).
- ⁴³ Dunfield, T. E., Wilson, W. H. and White, F. C., *Rubber and Plastics Age* 40, 1057 (1959).
- ⁴⁴ Howland, L. H., Aleksa, E. J., Brown, R. W. and Borg, E. L., *Rubber and Plastics Age* 42, 868 (1961).
- ⁴⁵ United States Rubber Company, Belgian Patent 592,204.
- ⁴⁶ Borg, E. L., Provost, R. E. and Bawn, C. V., *Ind. Eng. Chem.* 51, 278 (1955).
- ⁴⁷ Stoll, R. C., Blackwell, J. C. and Henry, P. J., *Ind. Eng. Chem.* 49, 1835-1837 (November, 1957).
- ⁴⁸ Grady, L. A., Mertz, C. W. and Fanning, R., *Ind. Eng. Chem.* 47, 2445 (1956).
- ⁴⁹ Daniel, W. and Otto, M., U. S. Patent 2,296,427, September 22, 1942.
- ⁵⁰ Gomm, A. S., U. S. Patent 2,313,144, May 9, 1943.
- ⁵¹ Leyonmark, G. F. and Arundale, E., U. S. Patent 2,595,797, May 6, 1952.
- ⁵² Ernst, J. L. and Betts, Jr., J. L., U. S. Patent 2,799,662, March 18, 1953.
- ⁵³ Aldridge, C. L. and Hunter, E. A., U. S. Patent 2,912,401, November 10, 1959.
- ⁵⁴ Brodkey, R. S. and Miller, A. L., U. S. Patent 2,936,295, May 10, 1960.
- ⁵⁵ Newberg, R. G., Miller, A. L. and Gilbert, W. J., U. S. Patent 2,928,759, March 15, 1960.
- ⁵⁶ Hunter, E. A., Segura, M. A., Small, A. B. and Miller, A. L., U. S. Patent 2,944,038, July 5, 1960.
- ⁵⁷ Brodkey, R. S. and Miller, A. L., U. S. Patent 2,966,094, October 4, 1960.
- ⁵⁸ Eby, L. T., Cottle, D. L. and Lemiska, T., U. S. Patent 2,958,667, November 1, 1960.
- ⁵⁹ Kelly, R. T. and Lewis, W. R., U. S. Patent 2,958,684, November 1, 1960.
- ⁶⁰ Saffren, G., *Plaste u. Kautschuk* 7, No. 9, 435 (1950).
- ⁶¹ Dallavalle, J. M., "Micromatics", Pitman Publishing Corporation, New York (1948).
- ⁶² Maron, et al., *J. Colloid Sci.* 10, 482 (1955), *ibid.* 494, *ibid.* 523 (1955), *ibid.* 11, 80 (1956).
- ⁶³ Johnson, P. H. and Kelsey, R. H., *Rubber World*, 138, 877-882 (September, 1958).
- ⁶⁴ Kelsey, R. H. and Johnson, P. H., *Rubber World* 139, 227-231 (November, 1958).
- ⁶⁵ Miller, A. L., "Viscosity Control in Butyl Latex" presented at the May, 1960, Buffalo, New York Meeting of the Division of Rubber Chemistry, ACS.
- ⁶⁶ Fryling, C. F. and Grindler, E. M., *Proc. Internat. Rubber Conf.*, Washington, D. C., November, 1959, pp. 456-466.
- ⁶⁷ Roe, C. F. and Brase, P. D., *J. Col. Sci.* 10, 194 (1955).
- ⁶⁸ Howland, L. H. and Nisonoff, A., *Ind. Eng. Chem.* 46, 2580-2586.
- ⁶⁹ Gliemers, F. A., Bennett, B., Stickney, P. B., Heiligmann, R. G. and de Decker, H. K. J. *RUBBER CHEMISTRY & TECHNOLOGY* 33, 535-544 (1960).
- ⁷⁰ Voyutskii, S. S. and Panich, R. M., *Uspekhi Khimii* 25, 57-90 (1956); *RUBBER CHEMISTRY & TECHNOLOGY* 31, 1140 (1958).
- ⁷¹ Van der Hoff, J. W., et al., *J. Polym. Sci.* 20, 225 (1956).
- ⁷² Berg, R. H., ASTM Special Technical Publication No. 234, 245 (1959).
- ⁷³ Schmidt, E. and Bidiaon, P. H., *Rubber Age* 88, 484 (1960); *RUBBER CHEMISTRY & TECHNOLOGY* 34, pages 433-445 (1961); cf. correction, 4th issue 1961.
- ⁷⁴ La Mer, V. K. and Plesner, I. W., *J. Polym. Sci.* 24, 147 (1957).
- ⁷⁵ Frants, G. C., Sanders, J. W. and Saunders, F. L., *Ind. Eng. Chem.* 49, 1449-1450 (1957).
- ⁷⁶ Brown, G. L., *J. Polym. Sci.* 22, 423-34 (1956).
- ⁷⁷ Howland, L. H., Peaker, C. R. and Holmberg, A. W., *India Rubber World* 579-581, 584 (1944).
- ⁷⁸ Rumbold, J. S., U. S. 2,414,394 (January 14, 1947).
- ⁷⁹ Dogadkin, B. A., Senatorakaya, L. G., Guseva, V. I., Suslykov, A. V. and Zakharchenko, P. I., *Colloid Journal (USSR)* 18, 523-530 (1956); *RUBBER CHEMISTRY & TECHNOLOGY* 31, 655-663 (1958).
- ⁸⁰ Goebel, H. L., Bargmeyer, E. G., Brase, P. D. and Mann, J. U., *Rubber World* 135-136, 421-428, (1956).

FLUORINE-CONTAINING ELASTOMERS

J. C. MONTERMOSO*

QUARTERMASTER RESEARCH AND ENGINEERING COMMAND, NATICK, MASS.

CONTENTS

	PAGE
I. Introduction.....	1521
II. Current objective in elastomer research.....	1522
III. Function of fluorine in the polymer molecule.....	1522
IV. The research on fluorine-containing elastomers.....	1524
V. Properties of fluorine-containing elastomers.....	1526
A. Fluorinated polybutadienes.....	1526
1. Polyfluoroprene.....	1526
2. Fluoroprene copolymers.....	1527
a. Dimethyl (vinylethynyl) carbinol-fluoroprene.....	1527
b. Styrene-fluoroprene.....	1527
c. Acrylonitrile-fluoroprene.....	1528
d. Chlorotrifluoroethylene-fluoroprene.....	1528
3. Polytrifluorobutadiene.....	1530
B. Vinylidene fluoride copolymers.....	1530
1. Chlorotrifluoroethylene-vinylidene fluoride.....	1531
2. Perfluoropropylene-vinylidene fluoride.....	1532
a. Fluorel.....	1534
b. Viton A and Viton A-HV.....	1535
C. Fluoroacrylate polymers.....	1537
D. Fluoropolyesters.....	1539
E. Fluorinated silicone elastomer.....	1540
F. Fluoropolyamidine.....	1542
G. Fluorinated nitroso elastomers.....	1542
1. Trifluoronitrosomethane-tetrafluoroethylene copolymer....	1542
a. Monomer synthesis.....	1543
b. Polymerization.....	1543
c. Vulcanization and properties.....	1545
2. Other nitroso copolymers.....	1548
VI. Discussion.....	1549
VII. Acknowledgment.....	1550
VIII. References.....	1550

I. INTRODUCTION

Fluoroprene, the first fluorine-containing elastomer, was developed by E. I. du Pont de Nemours & Company and reported by Mochel¹ and others in 1948. However, intensive research to develop specialty rubbers from fluorocarbons was not started until the early 1950's. At the time, there was an urgent

* The present address of Dr. Montermoso is the R. E. Darling Company, Inc., Washington, D. C.

military need for fuel and chemical resistant rubbers for service under extremely low temperatures. Consequently, most of the fluorine-containing elastomers were the result of research conducted or sponsored by the Department of Defense. Army experiences in the Aleutians during World War II and in several task force operations² in the Arctic regions showed, among others, that fuel hoses became brittle and cracked. Gaskets failed to function. On ship-board, the Navy was experiencing similar difficulties with rubber items. The Air Force³, on the other hand, was being plagued with an epidemic of fuel leakage on many of its aircraft. The extraction of the plasticizers from the nitrile rubber compounds and the low temperature of the environment caused shrinkage of the seals and gaskets resulting in leakage of fuels. Obviously, a solution to these problems was to develop new fuel resistant rubbers which would be inherently flexible at extremely low temperatures.

II. CURRENT OBJECTIVE IN ELASTOMER RESEARCH

In the early 1950's the original objective⁴ was to develop fuel and chemical resistant elastomers which would be serviceable at a range of temperature from minus 65° to plus 160° F. The operational requirements for rubber have multiplied within a decade. Tremendous changes in the development of new weapons systems have created additional and more stringent rubber requirements. New rubbers which will resist the concentrated acids, propellants, and potent oxidizers used in modern weaponry are urgently needed. Thermally stable elastomers at extremely high temperatures (above 1000° F) will continue to be a target for elastomer development. The military services also need elastomers that are highly resistant to the deleterious effects of flame for use in items or components that may be exposed to short-impulse, high-intensity heat and radiation⁵ from nuclear blasts. Materials now available burst into flame when exposed to nuclear blasts. The individual soldier is still the most indispensable part of our modern Army. If we can provide him, for example, with a uniform which will not flame, although it may decompose when exposed to such hazards, then we will have made a big step in protecting him. Admittedly, the functional requirements of the three military services may only differ in degree, intensity or severity due to differences of operations. Nevertheless, the current overall objective of military rubber research, applicable to all the services, is to develop elastomers possessing the following characteristics: (a) fuel and chemical resistance, (b) low temperature flexibility, (c) stability at high temperatures, (d) flame retardance or nonflammability, (e) radiation resistance, and (f) ozone and weather resistance. There are rubbers currently available which possess singly any of these characteristics. The desired elastomers, however, must have a combination of several of these properties. Significant progress has been made, although a great deal of research work still remains to be accomplished. Various areas or approaches have been investigated. Research on fluorine-containing compounds during the past decade offers the most promise.

III. FUNCTION OF FLUORINE IN THE POLYMER MOLECULE

Elemental fluorine does not occur free in nature, but its compounds are widely distributed in such minerals as cryolite (Na_3AlF_6) and fluorspar (CaF_2). It is the most reactive chemical element and combines directly and very vigorously with many substances. All attempts in its isolation failed until

Henri Moissan⁶, a 1906 Nobel Prize winner, obtained it by an ingenious method of electrolysis. The preparation of elemental fluorine by Moissan in 1886 is a significant event in the history of chemistry. Fluorine is prepared commercially by electrolysis of potassium hydrogen fluoride.

After World War II, the requirements for various materials, including elastomers, possessing the desired properties of chemical inertness, thermal stability and low temperature generated an intensive program on fluorine and fluorocarbon research. These properties which were found to be characteristic of organic fluorine compounds were responsible for the continuing emphasis in this field of investigation. Numerous fluorocarbon products have been produced and widely recognized during the last decade.

The fluorine atom imparts unusual characteristics when incorporated into the molecular structure of high polymers. Properties which can be directly attributed to the presence of the fluorine atom in the polymer molecule include heat and chemical resistance, flame retardance and electrical characteristics. Let us examine the possible causes for these phenomena.

There are many factors, such as forces between atoms and molecules, their sizes, and steric hindrance effects to which the properties of polymers are attributed. The forces acting in high polymers are of two kinds: (1) primary valence forces which are acting between atoms within the molecule and (2) secondary valence forces, frequently called Van der Waals forces which are acting between the molecules. The former forces are quite high; whereas, the latter are weak but very important.

Most of the physical properties of polymers are directly related to the intermolecular forces between the polymer molecules. These include viscosity, melting point, solubility and adhesion. Mechanical properties such as tensile strength and compression characteristics are basically related to the intermolecular forces, but can be altered by the method of synthesis which may affect, for example, the orderly arrangement or pattern of crystallinity of the polymer molecule. The secondary valence forces are the summation of a number of individual forces which are produced by residual fields left around the atoms. In general, the larger the polymer molecule, the more important these residual or intermolecular forces become.

In the fluorocarbons, the stability of the molecule greatly depends on the primary valence forces between carbon and fluorine. The bond energies⁸⁻¹¹ in kcal/per mole for radicals occurring in fluorocarbons are: 94 to 120 for C—F, 87 to 94 for C—H, 66 to 73 for C—Cl and 59 to 70 for C—C linkages. These figures show that fluorine forms a much stronger bond to carbon than those of either hydrogen, chlorine or carbon to carbon and hence imparts the highest order of stability. In highly fluorinated polymers such as Teflon, increased chemical inertness and thermal stability are attributed to a third factor, steric hindrance effects¹². The superior stability of the fluorocarbons is significant in contrast to that of the chlorocarbons. The "oversize" of the chlorine atom undoubtedly hinders the formation of long chain molecules in contrast to the "just right" size of fluorine. Brewster and McEwan¹³ state that attempts to prepare perchlorocarbons of the type C_nCl_{2n+2} where n is greater than 3 have failed. For example, chlorination of *n*-butane resulted in fragmentation of the molecule, yielding C_2Cl_4 and C_2Cl_6 , etc., instead of the desired decachlorobutane, C_4Cl_{10} . To date, there is no indication that polytetrachloroethylene ($-CCl_2-CCl_2-$)_n has been synthesized. Apparently, the chlorine atoms are so large that they produce a decided strain upon bonds and valence angles.

On the other hand, the smaller fluorine atoms fit snugly and uniformly around the carbon chain and form a protective shield which effectively prevents chemical attack on the weaker carbon to carbon linkages. The fluorocarbons have been described¹³ as having "hearts of diamond and skins of rhinoceros hide". The steric effect also applies, in a certain degree, to Kel-F polymers and to fluorinated nitroso elastomers which will be discussed subsequently.

Undoubtedly, there are other factors contributing to the various properties present in fluorine-containing polymers. The degree of bond saturation of the molecule has definite effects on the ability of the polymer to resist attacks from oxygen, ozone, acids, bases and other strong oxidizers. Flame resistance or nonflammability is a characteristic property of the halogens.

IV. THE RESEARCH ON FLUORINE-CONTAINING COMPOUNDS

The original objective of the military research which started about 1950 on fluorine-containing compounds was to develop chemical resistant elastomers which would be flexible and serviceable at Arctic and normal temperatures (-65° to 160° F). This was later extended in 1955 to include high temperature (500° F and up) elastomers. At the inception of the intensive research, two fluorocarbon polymers were outstanding: polytetrafluoroethylene (Teflon) and polychlorotrifluoroethylene (Kel-F, Genetron and Fluorothene). Both possess excellent chemical resistance and thermal stability. Although the first successful polymerization of polytetrafluoroethylene was discussed by Plunkett¹⁴ in 1941, its commercial production was described, including the polymer properties, by Renfrew and Lewis in 1946¹⁵. Brubaker¹⁶ and Joyce¹⁶ stated that tetrafluoroethylene can be polymerized readily under superatmospheric pressure and with suitable catalysts. Its average molecular weight ranges from 389,000 to 8,900,000 as discussed by Dolan¹⁷ and others. Polychlorotrifluoroethylene has been prepared by various methods and described in several patents^{18, 19}. The method of Dittman, Passino and Wrightson²⁰ is the commercial method employed by The M. W. Kellogg Company and subsequently by Minnesota Mining and Manufacturing Company. By this method the polymer is prepared in yields of up to 88% using distilled water as a diluent in concentration of 1 to 5 times the weight of the monomer. The pressure in these reactions is high enough to keep all reactants liquid and the reaction time is usually 5 to 35 hours. Rudner¹² summarized the properties of fluorocarbon resins as (1) capable of withstanding higher and lower temperatures than more complex resins, (2) chemically inert to both acids and alkali, (3) excellent moisture absorption characteristics, (4) better than average mechanical characteristics, and (5) excellent electrical properties. Teflon, in particular, is the only plastic material known where the "dielectric constant does not vary with temperature or frequency".

A decade ago, the possibility of developing fluorine-containing elastomers with the inherent properties of Teflon and Kel-F was exclusively a matter of faith with the optimistic few. Even the small but select group of fluorine experts had doubts as to the feasibility of synthesizing elastomers containing large quantities of fluorine in the molecule. Until the recent synthesis of a nitroso rubber, no vulcanizable elastomer existed that did not contain hydrogen atoms in the molecule. The substitution of fluorine for hydrogen in the olefins and dienes tended to produce plastic or resinous materials. For example, polyperfluorobutadiene is a plastic; polybutadiene, on the other hand, is an elas-

tomer. It is also known that polyvinylidene fluoride is a resin and polychlorotrifluoroethylene is a plastic; however, copolymers of the monomers of these two plastic materials produced good elastomers (Kel-F Elastomers 3700 and 5500) which are now commercially available.

With the above setting as background, the Quartermaster Corps, U. S. Army, initiated in 1950 a research project with The M. W. Kellogg Company who was at the time producing and marketing Kel-F plastic and various waxes and oils obtained from chlorotrifluoroethylene derivatives. This QMC project, directed toward developing chemical-resistant low-temperature rubbers from fluorinated compounds, was continued by Minnesota Mining and Manufacturing Company in 1957 when it purchased the Chemical Division of The M. W. Kellogg Company. Almost simultaneously with The M. W. Kellogg Company contract, two projects on the synthesis of fluorine-containing monomers were initiated by the Quartermaster Corps; one with the University of Florida, which is still in effect, and the other with Ohio State University. The monomers synthesized by the universities were delivered to Minnesota Mining and Manufacturing Company for polymerization. The resulting elastomers were then sent to the Quartermaster Corps Laboratories for evaluation, screening, vulcanization and compounding studies. The above team was expanded in 1958 to include the University of Colorado for the purpose of synthesizing novel fluorine-containing monomers. Several outstanding elastomers have been developed by this team from industry, universities and government laboratories. To date, about 150 monomers have been covered by this investigation. More than 500 fluorocarbon-based copolymer systems have been explored of which approximately 175 systems resulted in elastomeric materials.

At about the same time, the Air Force initiated a research contract with Minnesota Mining and Manufacturing Company on fluorocarbons with emphasis on fluoroacrylates. The choice seemed appropriate since Minnesota Mining and Manufacturing Company had already in operation an electrochemical fluorination method known as the Simons process. The Air Force contract with Minnesota Mining and Manufacturing Company was terminated in 1957. The Air Force also sponsored monomer synthesis projects with several universities including Purdue, Duke, Florida and Pennsylvania State. Later on, the Air Force initiated contracts with Hooker Electrochemical Company and Peninsular Chem-Research, Inc. Several elastomers produced under Air Force sponsored research will be discussed. It might be apropos to mention that concurrent with the work of the Army and Air Force, basic research on fluorine was extensively being investigated by the Office of Naval Research, U. S. Navy²¹. It would be amiss not to recognize the efforts and contributions of segments of industry, such as E. I. du Pont de Nemours and Company, Dow Corning Corporation and others who were undertaking the investigation on their own, without government or military services support. The results of their efforts, which are offered and always available to military applications, will be evident later in this discussion.

It would be practically impossible to present in this brief review all the fluorine-containing elastomers, which in the majority of cases, have been made in gram quantities only. Consequently, only the outstanding ones will be discussed in detail; those elastomers which have been produced commercially or at least in pound quantities and whose chemical and physical properties have been conclusively determined in the vulcanizate.

V. PROPERTIES OF FLUORINE-CONTAINING ELASTOMERS

A. FLUORINATED POLYBUTADIENES

The substitution of fluorine for hydrogen in hydrocarbons containing 1 to 5 carbons, with particular emphasis on dienes and olefins and their derivatives, was a logical start from which to prepare fluorine-containing elastomers. Lovelace, Postelnek and Rausch²² made a comprehensive summary of aliphatic fluorocarbon synthesis.

1. *Polyfluoroprene*.—Polyfluoroprene is the first fluorinated elastomer which has been investigated quite extensively. It is the homopolymer of 2-fluorobutadiene-1,3 which was developed by E. I. du Pont de Nemours Company. The synthesis of fluoroprene, reported in a number of patents²³⁻²⁹ was accomplished by the gas phase addition of anhydrous hydrogen fluoride to monovinylacetylene in the presence of nitrogen. The monovinylacetylene is made by the dimerization of acetylene, according to Nieuwland³⁰. The patent literature contains information on its polymerization³¹⁻³⁵ which is generally by the persulfate-mercaptan water emulsion method. Modifications of this method have been made. Several investigators summarized the properties and synthesis of the polymer^{1, 36}. Valuable polymerization data were supplied by Orr and Williams³⁷ who also showed that the molecular structure of polyfluoroprene is a random combination of 1,2 addition, 3,4 addition and *trans*-1,4 head to tail linkage. This is distinctly different from polychloroprene (neoprene) which is almost 100% *trans*-1,4 head to tail chain structure.

TABLE I
PROPERTIES OF POLYFLUOROPRENE TREAD STOCK COMPOUND

Polyfluoroprene	100	Tensile strength, psi	2900
MPC black	40	Elongation %	400
Phenyl-1-naphthylamine	2	Modulus (300%), psi	1650
Stearic acid	1	Hardness, Shore A	72
Zinc oxide	10	Rebound, Schopper, %	44
XLC magnesia	10	Tear resistance, lb/inch	210
Sulfur	2		
Cure: 60 minutes @ 153° C			

In most of its physical and chemical properties, reported by Mochel and others³⁸, polyfluoroprene occupies a position between polychloroprene and randomized polybutadiene synthesized by redox emulsion method. Like polybutadiene, it requires filler reinforcement to develop high tensile strength. The oil resistance, tested in kerosene, is similar to that of polychloroprene (neoprene) but its resistance to sunlight and ozone is not as outstanding. The low temperature flexibility compares favorably with neoprene behavior. While neoprene self-extinguishes a flame, polyfluoroprene propagates a flame when ignited but it burns at a much slower rate than polybutadiene or natural rubber. It is superior, however, to neoprene in electrical properties, approaching natural rubber in resistivity and power factor. The density of polyfluoroprene is 1.13 compared with neoprene of 1.23, natural rubber of 0.93, and nitrile rubber of 1.00³⁹. In polymerization behavior, fluoroprene polymerizes approximately 25 times faster than butadiene under comparable conditions but slower than chloroprene. Fluoroprene copolymerizes readily, like butadiene, in wide proportions with most dienes and olefins. Chloroprene, on the other hand, does not copolymerize readily with many monomers.

TABLE II
COMPARISON WITH OTHER ELASTOMERS

	Polyfluoro- prene	Neoprene FR	Natural rubber	Nitrile 75/25	SBR
Volume swell, %	75	95	200	24	200
TR10, °C	-48	-39	-44	—	-49

Polyfluoroprene is easily vulcanized in gum or filler-reinforced stocks. A typical tread stock formulation in parts by weight and the properties of the vulcanizate are shown in Table I.

At 70° C (158° F), tensile strength of the above stock was 1850 psi and ultimate elongation was 400 per cent. After oven aging for 24 hours at 121° C, the vulcanizate retained 56% (1620 psi) of its original tensile strength and 45% of the elongation.

Polyfluoroprene was compared with other elastomers for oil resistance and low temperature flexibility. The samples were immersed in kerosene for 48 hours at 100° C and the volume swell determined. There is a direct relationship⁴⁰ between degree of swelling and loss of tensile strength and other properties. To determine low temperature flexibility, the rubber samples were stretched and held in clamps and then subjected to an atmosphere of minutes 70° C. The clamps were then released, and the temperature gradually raised. The temperature at which the sample retracted 10% (TR10)⁴¹ of the original stretch was determined. The results are shown in Table II.

After immersion in boiling water for 48 hours, polyfluoroprene vulcanizates generally exhibit 5 to 6% volume increase.

2. *Fluoroprene copolymers.*—Fluoroprene copolymerizes readily with most dienes and olefins. Orr and Williams³⁷ investigated its copolymerization characteristics with styrene, 2-methylstyrene, methyl methacrylate, isoprene and acrylonitrile at 50° C using the butadiene copolymerization formula developed by Gilbert and Williams⁴². Mochel¹ and others did a great deal of research on the copolymerization of fluoroprene at various comonomer ratios and determined the properties of the vulcanizates.

a. *Dimethyl(vinylethynyl)carbinol-fluoroprene.*—Vulcanizates of copolymers with dimethyl(vinylethynyl)carbinol showed improvement in tensile strength and more significantly in mill processing. As the proportion of the carbinol increased, there was an increase in oil resistance accompanied by a decrease in low temperature flexibility, as determined from the vulcanizate, Table III.

b. *Styrene-fluoroprene.*—The styrene copolymers of fluoroprene are less oil resistant than the corresponding dimethyl(vinylethynyl)carbinol copolymers and do not process as easily. The tensile strength is superior to polyfluoroprene, but compares unfavorably in oil resistance and low temperature flexibility, Table IV.

TABLE III

PROPERTIES OF DIMETHYL (VINYLETHINYL) CARBINOL-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	80/20	75/25
Tensile strength, psi	2900	3410	3530	3610	2950
Elongation, %	400	475	520	480	380
Volume increase*, %	75	74.5	69.5	61.0	48.6
TR10, °C	-48	-46.9	-40.2	-33.5	-27.0

* 48 hours immersion in kerosene at 100° C.

TABLE IV
 PROPERTIES OF STYRENE-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	85/15	75/25
Tensile strength, psi	2900	3580	3320	4090	3320
Elongation, %	400	500	425	520	500
Volume increase*, %	75	102	100	97.3	92.8
TR10, ° C	-48	-46	-42	-38	-29

* 48 hours immersion in kerosene at 100° C.

c. *Acrylonitrile-fluoroprene*.—Greatly improved oil resistance and tensile strength are obtained from the copolymers of fluoroprene and acrylonitrile at the sacrifice of low temperature flexibility, Table V. The copolymers with high acrylonitrile content tend to be dry and difficult to process without the use of softeners and plasticizers.

Terpolymers of fluoroprene-acrylonitrile-butadiene have also been synthesized. Some of these showed high oil resistance and some superior low temperature flexibility depending upon the monomer ratios of the terpolymer.

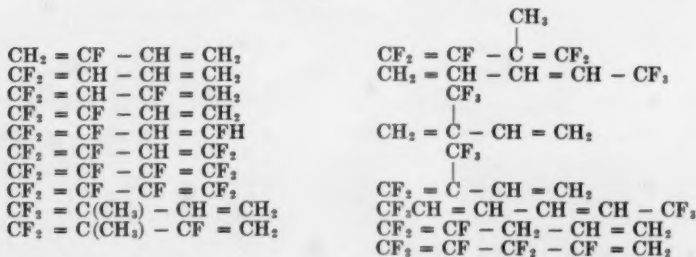
 TABLE V
 PROPERTIES OF ACRYLONITRILE-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	85/15	75/25
Tensile strength, psi	2900	3070	3480	4090	4460
Elongation, %	400	390	380	520	400
Volume increase*, %	75.0	58.5	31.1	23.9	15.0
TR10, ° C	-48.0	-46.0	-37.1	-32.6	-23.0

* 48 hours immersion in kerosene at 100° C.

In over-all properties, the terpolymers showed little or no improvement over the copolymers or homopolymers. Starkweather²⁶ and others also copolymerized fluoroprene with butadiene.

d. *Chlorotrifluoroethylene-fluoroprene*.—Hoyt⁴³ investigated the copolymerization of fluoroprene with chlorotrifluoroethylene. The polymerization reaction was carried out in the presence of a free-radical forming initiator. This was done by using water-soluble peroxy-type initiators, as potassium persulfate, in a water-suspension type recipe or halogen-substituted organic peroxides, as trichloroacetyl peroxide, in bulk type system.

 TABLE VI
 FLUORINATED DIENE MONOMERS


The meager data on this copolymer system was obtained from molded unvulcanized samples. For a copolymer containing 93 mole per cent of fluoro-prene and 7 mole per cent of chlorotrifluoroethylene, the low temperature characteristics are shown by the Gehman values: T_2 -minus 5° C, T_5 -minus 12° C, T_{10} -minus 16.5° C and T_{100} -minus 27° C. (Gehman values measure the stiffness of the elastomer at various temperatures. For example, T_2 indicates the temperature at which the elastomer becomes twice as stiff as it is at room temperature (25° C); T_5 means five times as stiff, etc.). Its volume increase, after 48 hours immersion in a mixed solvent of 40% toluene (ASTM

TABLE VII
COMPARISON OF PROPERTIES OF POLYTRIFLUOROBUTADIENE (PTFB) WITH
THOSE OF NEOPRENE AND NITRILE RUBBERS

	Formulations—parts by weight		
	PTFB	Neoprene	Nitrile
Polytrifluorobutadiene	100.0		
Neoprene		100.0	
Nitrile (Hycar 1001)			100.0
Stearic acid	0.5	0.5	0.5
Zinc oxide	5.0	5.0	5.0
Carbon black (Philblack-O)	30.0	40.0	40.0
Plasticizer (TP90B)	10.0	10.0	10.0
Dicumyl peroxide	4.0		
XLC		2.0	
Tetramethyl thiuram monosulfide		1.0	
Benzothiazyl disulfide			1.5
Sulfur		1.0	1.5
Optimum cure: min/° F	30/307	30/307	30/307
<i>Original Properties of Vulcanizate</i>			
Tensile strength, psi	2600	2400	2800
Elongation, %	380	340	390
Modulus, 300% elongation	1700	2100	1700
Hardness, Shore A	52	61	58
<i>After 48 Hours Immersion in ASTM Type III Fuel*</i>			
Volume increase, %	16	65	19
Tensile strength, psi	1700	750	1550
Tensile loss, % of original	34.6	68.8	44.7
<i>Low Temperature Flexibility Tests</i>			
Gehman relative stiffness: T_2 ° C	-27	-32	-17
T_5	-36	-37	-20
T_{10}	-38	-39	-22
T_{100}	-43	-45	-26
Temperature retraction: TR10° C	-36	-44.3	-27.7
TR30	-14	-34.9	-23.1
TR50	+2.4	-20.5	-20.2
TR70	+12.0	-2.0	-16.4
<i>Compression Set at Various Temperatures, 30 Minutes after Release of Compression</i>			
After 70 hrs @ 212° F in air oven, %	15.6	69.0	72.3
After 24 hrs @ -30° F, %	86.0	62.8	97.5
After 7 days @ -30° F, %	91.0	62.0	99.0

* 70:30 mixture of isooctane and toluene.

Type II Fuel) and 60% by volume of isooctane was 69.1%. Copolymerization of fluoroprene with tetrafluoroethylene also resulted in rubbery products.

The overall properties of the homopolymer and copolymers of fluoroprene did not show significant advantages over neoprene and nitrile rubbers.

3. *Polytrifluorobutadiene*.—This elastomer is really not a homopolymer, but a 40:60 copolymer of 1,1,2 and 1,1,3 trifluorobutadienes. The fluorinated dienes which received considerable attention under the Army Quartermaster Corps Rubber Research Program are shown in Table VI⁴.

Fluoroprene, the first on the list, was relatively easy to synthesize from the reaction of hydrogen fluoride and monovinyl acetylene. The difluoro and trifluoro derivatives of butadiene and isoprene were much more difficult to make and in many cases, entirely new methods of synthesis had to be developed. The 1,1,2 and 1,1,3-trifluorobutadiene monomers were synthesized by Prof. Tarrant⁴⁵ and his staff at the University of Florida. The polymerization was carried out by Dr. Copenhaver⁴⁶ and his group at the M. W. Kellogg Company and subsequently at Minnesota Mining and Manufacturing Company. Almost all these monomers homopolymerized and copolymerized readily to produce rubbery materials. Perfluorobutadiene, however, reacted with difficulty and its homopolymer was a powdery product. The perfluoroisoprene, using the regular emulsion recipe, did not homopolymerize.

The homopolymers of 1,2,3 and 1,1,3-trifluorobutadienes were made but the copolymer had overall properties superior to either of the homopolymers. Although the copolymer did not reach commercial production, approximately 40 pounds of the elastomer had been produced for extensive vulcanization and compounding research. The physical and chemical properties⁴⁸ of the copolymer presented here, (Table VII) are unpublished data from the laboratories of the Quartermaster Research and Engineering Command.

The data show that the polytrifluorobutadiene is as oil resistant as nitrile rubber and definitely superior to neoprene. In low temperature characteristics, it is equal to neoprene and superior to nitrile rubber in relative stiffness; however, it is inferior to both rubbers in the ability to retract at low temperatures. In compression set properties, polytrifluorobutadiene is superior to neoprene and nitrile rubber at high temperatures; however, at subzero temperatures, it is slightly better than nitrile rubber, but inferior to neoprene. Its overall properties did not show significant advantages over neoprene or nitrile rubber to warrant its commercial production, which is estimated to be several times as costly.

B. VINYLIDENE FLUORIDE COPOLYMERS

Of the many fluorinated olefins investigated, the following have shown the most promise: vinylidene fluoride, $\text{CH}_2=\text{CF}_2$; chlorotrifluoroethylene, $\text{CFCl}=\text{CF}_2$; perfluoropropylene, $\text{CF}_3-\text{CF}=\text{CF}_2$; and tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$.

Vinylidene fluoride copolymerized readily with other monomers resulting in rubbery materials. The fluorine present as CF_2 provided chemical resistance and the CH_2 contributed to the chain flexibility and freedom of segmental rotation. Vinylidene fluoride is described by Swarts⁴⁹ as "a colorless, odorless gas—not oxidized in air and not polymerized by sunlight." McBee, Hill and Bachman⁵⁰ obtained vinylidene fluoride by dechlorination of 1,1-difluoro-1,2-dichloroethane by zinc in acetamide solution. Other methods of monomer synthesis have been reported^{51, 52}. Both the monomer and the homopolymer

are available commercially from Allied Chemical and Dye Corporation and Pennsalt Chemical Corporation. Like other fluorinated plastic materials, polyvinylidene fluoride is resistant to most corrosive chemicals and solvents and possesses a high degree of thermal stability.

1. *Chlorotrifluoroethylene-vinylidene fluoride copolymers.*—The first elastomer developed under the QMC Rubber Program and commercially produced by the M. W. Kellogg Company and currently by Minnesota Mining and Manufacturing Company was a 50:50 (mole ratio) copolymer of chlorotrifluoroethylene and vinylidene fluoride. This was designated as X-300 and later was given a trade name of Kel—F Elastomer 5500. In an effort to improve the low temperature flexibility and the tensile strength, another elastomer containing 30 mole % of chlorotrifluoroethylene and 70 mole % of vinylidene fluoride was developed, and was designated as Kel—F Elastomer 3700. Robb, Honn and Wolf⁵³ determined the properties of the unvulcanized gums, shown in Table VIII.

Griffis and Montermoso⁵⁴ reported that the Kel—F Elastomers could be vulcanized by peroxides, diisocyanates, or amines, preferably hexamethylene diamine carbamate. No vulcanization was effected by sulfur-containing com-

TABLE VIII
GUM PROPERTIES OF KEL-F ELASTOMERS

Properties	Type 5500	Type 3700
Specific gravity	1.85	1.85
Per cent fluorine by weight	Approx. 54	Approx. 56
Color	off-white	off-white
Hardness, Shore A	45	45
Embrittlement temperature, °C	-51	-64
Tensile strength, psi	350-600	350-600
Low temperature, Gehman °C, T ₂	+7	-7
T ₈	+3	-11
T ₁₀	+1	-14
Processibility on the mill at 120° F	good	poor
Processibility on the mill at 170° F	good	good

pounds. These elastomers also responded to vulcanization by gamma radiation. Jackson and Hale⁵⁵ found that a dose of 10 megareps crosslinked a black-loaded stock of Kel—F Elastomer 5500 to produce a tensile strength of 1530 psi. Numerous diisocyanates, peroxides and amines have been investigated. The diisocyanates, particularly toluene-2,4-diisocyanate and methylene-bis(4-phenylisocyanate), were effective in vulcanizing the Kel—F Elastomers. However, the vulcanizates were less acid-resistant than the peroxide vulcanizates. Although the peroxide cures, in general, produced higher tensile strength than those of the amine cures, their vulcanizates were less heat and chemical resistant. The amines produced good overall results if properly handled. The amines were difficult to incorporate into the stock during mixing on the mill. It was practically impossible to incorporate 1 or 2 parts (per 100 parts of rubber) of triethylene tetramine, for example, without serious scorching. To date, the generally used curing system of Kel—F Elastomers is the inner salt of hexamethylene diamine carbamate (HMDA—C) which has the structure $\text{NH}_3^+(\text{CH}_2)_6\text{NHCO}_2^-$. It processes satisfactorily on the mill and imparts good physical properties to the vulcanizate. Silicone oxide is the best reinforcing filler for Kel—F Elastomers. Table IX shows a typical basic formulation.

TABLE IX
BASIC FORMULATION FOR KEL-F ELASTOMERS

Kel-F Elastomer	100
SiO ₂ (Hi-Sil)	10
Zinc oxide	5
Dibasic lead phosphite (Dyphos)	10
HMDA	3
Press cure: 30 min @ 320° F	
Post oven cure: 16 hrs @ 350° F	

The Kel—F Elastomers have tensile strengths of 2500 and 3000 psi and an elongation of approximately 400% based on the above formulation. The physical properties of Kel—F Elastomers 5500 and 3700 are practically the same except that the latter is slightly superior⁵⁶ in low temperature flexibility and in resistance to hydrocarbon fuels as shown in Table X.

Conroy⁵⁷ and others showed that the Kel—F Elastomers possessed good chemical resistance and were superior in thermal stability to any oil and fuel resistant rubbers commercially available at the time. Headrick⁵⁸ found that properly compounded stocks of Kel—F Elastomers showed outstanding resistance to hydraulic fluids at temperatures up to 400°F. Smith⁵⁹ and others also reported that properly compounded stock of Kel—F Elastomers retained good physical properties after 500 hours at 400° F in JP-5 fuel (approx. 15% aromatics). At about this time, the Air Force's need for high temperature elastomers, due to the development of high speed aircrafts and high temperature hydraulic fluids, was accentuated. These findings and reports by other investigators led to a request from the Air Force to the Quartermaster Corps to include in the QMC objective the development and evaluation of thermally stable elastomers. The scope of the QMC research projects with the M. W. Kellogg Company and the University of Florida was therefore expanded to include development of fluorinated elastomers stable at 500° F and higher⁶⁰. A considerable number of compounding studies⁶¹⁻⁶³ directed toward varied applications, such as O-rings, hose, seals, gaskets and tanks, revealed not only the desirable qualities but also some deficiencies of Kel—F Elastomers. For high temperature seals and gaskets, the Kel—F Elastomers found limited service due to poor resistance to compression set. They could not be used for service at subzero temperatures.

2. *Perfluoropropylene-vinylidene fluoride copolymers.*—Copolymers of perfluoropropylene and vinylidene fluoride have produced elastomers with outstanding stability and chemical resistance. The researches responsible for the development of these copolymers were carried out independently by the M. W. Kellogg Company under QMC sponsorship and by E. I. du Pont de Nemours Company without any government financial support. The Kellogg elastomer is a 30:70 copolymer of perfluoropropylene and vinylidene fluoride. In the experimental stage of development, it was designated as Fluorocarbon Elastomer 214. Currently, it has a trade name of Fluorel, produced by Minnesota Mining

TABLE X

Tests	Elastomer 5500	Elastomer 3700
Low temperature, Gehman T _h , °C	+32	+7
Volume increase*, %	30	14

* Immersed in 70:30 isooctane-toluene for 7 days at 25° C.

and Manufacturing Company. Fluorel is an improved version of Fluorocarbon Elastomer 214. The du Pont polymer is known as Viton A and Viton A-HV is a modification of Viton A. Both Fluorel and Viton are prepared by water emulsion polymerization using potassium persulfate initiation. However, for emulsifying agent du Pont uses ammonium perfluorooctanoate⁶⁴ and Minnesota Mining and Manufacturing Company uses perfluorooctanoic acid. There may also be minor differences in conditions of polymerization such as temperature

TABLE XI
COMPARISON OF ELASTOMERS 214 AND 3700
(HMDA-Carbamate Cure)

Original physical properties	Type 214	Type 3700
Tensile strength, psi	1710	2640
Elongation, %	265	395
Hardness, Shore A	65	65
Low temperature properties		
Gehman torsional, T ₂ , °C	-5	-9
T ₅	-9	-14
T ₁₀	-11	-16
T ₁₀₀	-16	-23
Temp. retraction, TR10, °C	-16	-16
TR30	-13	-6
TR50	-11	+1
TR70	-8	+7
Volume increase in test fluids after 48 hrs @ 25° C, %		
In 70:30 isooctane-toluene	0	4
In Turbo Oil 15 (diester oil)	0	49
Tensile strength after 5 hrs in air, psi		
at 400° F	1660	2480
500° F	1480	1150
550° F	1310	950
600° F	1120	—
Tensile strength after 70 hrs in air, psi		
at 400° F	1700	1320
500° F	1000	480
550° F	440	—
600° F	—	—
Tensile strength after 5 hrs in Turbo Oil, psi		
at 400° F	1670	540
500° F	1400	80
Tensile strength after 70 hrs in Turbo Oil, psi		
at 400° F	1770	160
500° F	630	—
Tensile strength after 5 hrs in MLO 8200*, psi		
at 400° F	1690	2490
500° F	1510	1160
550° F	1110	600
600° F	870	—
Tensile strength after 70 hrs in MLO 8200*, psi		
at 400° F	1630	1660
500° F	440	—
550° F	—	—

* Silicate ester oil.

We know that polyvinylidene fluoride exists as a plastic and that perfluoropropylene does not homopolymerize^{65, 66}; therefore, no matter how high a ratio of perfluoropropylene is present in the initial feed, the composition of the resulting polymer will not exceed 50 mole per cent of perfluoropropylene.

Fluorel and Viton elastomers can be vulcanized by peroxides and amines. In general, they possess similar properties.

a. Fluorel.—The development of Fluorel was started as early as 1953. However, its properties were not reported until 1955⁶⁷⁻⁶⁹. Fluorel vulcanizates cured with benzoyl peroxide exhibited higher tensile strength than those of the HMDA-Carbamate; however, the latter possess better balance of physical properties, including heat resistance and compression set. Wilson, Griffis, and Montermoso^{70, 71} compared Fluorocarbon Elastomer 214 and Kel-F Elastomer 3700 in thermal stability and in resistance to various solvents and liquids. Based on the basic formulation of Table IX with minor modifications, the result of the comparison is shown in Table XI.

Fluorocarbon Elastomer 214 showed superiority in its resistance to diester oil and to hydrocarbon fuels. Its stability at high temperatures both in air and in hydraulic liquids, particularly in diester oil, is a marked improvement over the Kel-F Elastomers. This is supported by the results on volume increase

TABLE XII
RAW GUM PROPERTIES OF FLUOREL

Specific gravity	1.85
Fluorine content, wt %	>60
Color	off-white
Mooney viscosity, ML-4/212° F	135
Embrittlement temperature, ° F	-50
Gehman torsional, T_3 , ° F	+15
	T_5
	+5
	T_{10}
	+2
Storage stability	excellent
Solubility	esters and ketones

at 25° C after 48 hours immersion. The Gehman stiffness test indicates a slight superiority in low temperature flexibility for Kel-F Elastomer 3700. The temperature retraction test, on the other hand, shows a slight superiority for Fluorocarbon Elastomer 214. Neither are suitable for use below 10° C. Bovey⁷² presented some data on the vulcanizates cured with benzoyl peroxide. In general, the results were comparatively similar to those of the HMDA-carbamate vulcanizates.

Several modifications and improvements have been made on Fluorocarbon Elastomer 214. Subsequently, it was also designated as Kel-F Elastomer 2140. Admittedly, this is a misnomer, since the elastomer does not contain chlorotrifluoroethylene or Kel-F monomer. Currently, the improved elastomer with maximum heat resistant properties is known as Fluorel. Stivers, Honn and Robb⁷³ made a comprehensive evaluation of Fluorel. The raw gum properties of Fluorel are shown in Table XII.

Several Fluorel compounds, designed to meet the performance requirements of Specification MIL-R-25897-A-Rubber, have been developed by Stivers, Peterson and Meier⁷⁴. Medium thermal carbon black, Thermax, was used for easy and smooth processing; magnesium oxide, (Maglite K,) for maximum heat resistance; and a combination of HMDA-carbamate and copper Inhibitor

TABLE XIII
HEAT RESISTANT FLUOREL COMPOUNDS

Fluorel Elastomer	100	100
Carbon black (Thermax)	15	15
MgO (Maglite K)	20	20
HMDA-carbamate	1	1.4
Copper Inhibitor No. 65	—	0.2
Press cure: 30 min/300° F; post oven cure: 24 hrs/400° F		
Original Properties		
Tensile strength, psi	2400	2340
Elongation, %	310	225
Hardness, Shore A	68	71
After Aging, Tensile Strength Retention, %		
Air aged 16 hrs/600° F	56	73
72 hrs/400° F in MIL-0-8200	85	91
72 hrs/400° F in Anderol L-774	81	87
72 hrs/77° F in Ref Fuel B	80	92
Compression Set (ASTM Method B), %		
70 hrs/250° F	18	9
70 hrs/350° F	30	30
70 hrs/400° F	42	47
22 hrs/450° F	52	61

No. 65 (active ingredient disalicyl propylenediamine) for improved aging properties. Table XIII shows two typical formulations, with and without Copper Inhibitor No. 65, and some properties of Fluorel compounds.

b. *Viton A and Viton A-HV*.—E. I. du Pont de Nemours Company announced in 1956 the development of Viton A. Dixon, Rexford, and Rugg⁷⁶ reported its unusual thermal stability and resistance to fuels, lubricants and hydraulic fluids at ordinary and elevated temperatures. Other investigators^{76, 77} have confirmed these findings. Viton A, like Fluorel, can be vulcanized by peroxides, amines and high energy radiation. Vulcanizates from HMDA-Carbamate have the best combination of chemical and physical properties. Compounding studies⁷⁸⁻⁸², covering reinforcement and vulcanization, have improved the properties of Viton A vulcanizates. Griffin^{83, 84} has developed a technique for room temperature vulcanization for Viton A compounds. Smith⁸⁵ studied the chemistry of vulcanization of Viton A. He also reported⁸⁶ that dithiol-cured Viton A has high tensile strength, low compression set and good aging characteristics.

In addition to changes in compounding, the properties can be improved by polymer modifications. Gallagher, Eubank and Moran⁸⁷ discussed the prop-

TABLE XIV
RAW GUM PROPERTIES OF VITON POLYMERS

	A	A-HV
Specific gravity	1.8	1.8
Mooney viscosity, ML-4/212° F	75	170
Molecular weight (Mn)	100,000	200,000
Appearance	white, translucent	
Storage stability	excellent	
Solubility	good in ketones	

TABLE XV
PROPERTIES OF VITON VULCANIZATES

Polymer	100	
MT carbon black	25	
Magnesium oxide	15	
HMDA-Carbamate	1.5	
Press Cure: 30 min @ 300° F; oven step-up cure: 1 hr. steps @ 212, 300 and 350° F followed by 24 hrs @ 400° F		
Original properties	A	A-HV
Tensile strength @ 75° F, psi	2250	2725
Elongation @ 75° F, %	180	190
Hardness, Shore @ 75° F	71	71
Tensile strength @ 300° F, psi	550	720
Elongation @ 300° F, %	90	90

erties of Viton A-HV which is the improved version of Viton A. Viton A-HV has higher molecular weight, increased tensile strength and is less susceptible to blistering of the vulcanizate when used in high temperature applications. The properties of the unvulcanized uncompounded rubber are shown in Table XIV.

Note that Viton A-HV has a molecular weight twice that of Viton A. Table XV shows the typical formulation for Viton elastomers and the properties of the two types. The aging properties of Viton A-HV are given in Table XVI.

Viton A-HV, like Viton A, has excellent solvent resistance. The values in parenthesis after the various fluids in Table XVI represent the volume increases in per cent after 7 days at the specified temperatures.

Gallagher, Eubank and Moran⁸⁷ also investigated the problem of blistering in high-temperature, high-pressure hydraulic hose made of Viton A elastomer. It seemed that one of the fundamental causes of blistering was the relatively high solubility of gases in Viton A coupled with extremely low diffusion rates. Under high pressure the low diffusion rate permits compression of any gas present in the rubber stock. The compressed gas can presumably collect in tiny voids in the rubber and blister when the pressure exceeds the tensile strength and/or tear strength. The solubility and diffusion rates of various gases through a vulcanized Viton A gum stock were determined. The solubilities decreased in the order $\text{CO}_2 > \text{N}_2 > \text{He}$ and the rate of diffusion increased in the order $\text{CO}_2 < \text{N}_2 < \text{He}$. Maximum blistering, therefore, should occur with CO_2 . Blister-free stocks have been developed from Viton A-HV by the use of a particular type of MgO , "Maglite D", and a special additive, N,N'-bis-o-

TABLE XVI
AGING PROPERTIES OF VITON A-HV

Original tensile strength retained, %	
After 28 days in oven at 450° F	80
After 6 hours in oven at 600° F	67
After 7 days immersion in various fluids	
Petroleum aircraft fuel at 75° F	100 (0.4)
ASTM #3 oil at 300° F	95 (4.3)
Turbo Oil 15 at 400° F	60 (19.6)
Benzene at 75° F	73 (19.6)
Conc. NaOH 47% at 75° F	75 (2.1)

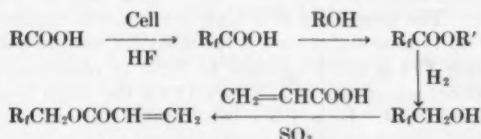
hydroxybenzylidene)-1,2-propylenediamine. The exact role of the additive was not completely understood. The blistering test was done in an autoclave using Turbo Oil No. 15 at 400° F and with nitrogen pressure of 1000 to 1400 psi for one hour.

Undoubtedly the elastomers obtained from copolymerization of perfluoropropylene and vinylidene fluoride, both Fluorel and Viton, will find many military and civilian applications due to the excellent combination of their high thermal stability and unusual solvent resistance.

Other copolymer systems, with vinylidene fluoride have been tried. For example, tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$, has been successfully copolymerized⁸⁸ with vinylidene fluoride, resulting in a flexible plastic material at ordinary room temperature. It became rubbery at approximately 250°F. It was thermally stable up to 650° F; however, on standing overnight at 700° F, the polymer decomposed leaving no residue.

C. FLUOROACRYLATE POLYMERS

Emphasis of the fluorocarbon elastomer research at Minnesota Mining and Manufacturing Company, under the Air Force sponsorship, was on fluorinated olefins and dienes, vinyl esters of fluorocarbon acids, acrylate esters of fluorinated alcohols, perfluoroacrylonitrile, and perfluoroamines. The Fluoro-Rubber Research at 3M from 1949 to 1957 was reviewed by Abern⁹⁰. The esters of acrylic acid with 1,1-dihydroperfluoroalcohols were found to be the most promising class of monomers from which rubbery polymers and copolymers were prepared. Synthesis of the 1,1-dihydroperfluoroalkyl acrylate monomers is schematically shown:



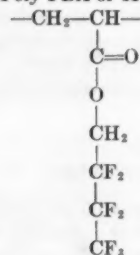
The first step shown above is the electrofluorination of a carboxylic acid by Simons⁹⁰ process. The symbol R_f denotes any fluorinated alkyl group. The most practical and preferred polymerization method for the acrylates was by water-emulsion persulfate system. Coagulation of the latex was by freezing

TABLE XVII
PROPERTIES OF FLUOROACRYLATE ELASTOMERS

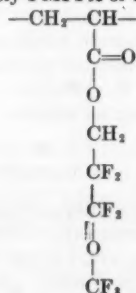
Fluoroelastomer	100		
Carbon black (Philblack O)	35		
Triethylene tetramine	1.25		
Sulfur	1.0		
Cure: 30 min at 310° F			
	1F4	2F4	NBR
Tensile strength, psi	1200	1000	4000
Elongation, %	360	400	470
Gehman, T ₁₀ , ° C	-7	-30	-13
Volume increase, %			
70:30 isooctane-toluene	17	15	33
Benzene	26	19	160

or by the addition of electrolytes. Considerable number of homopolymers of the acrylate series have been synthesized and their properties determined. The fluoroacrylates which possessed the best combination of physical and chemical characteristics were poly 1,1-dihydroperfluorobutyl acrylate (Poly FBA or 3M Brand Fluoro-Rubber 1F4) and poly perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate (Poly FMFPA or Fluoro-Rubber 2F4). Their molecular structures are as follows:

Poly-FBA or 1F4



Poly-FMFPA or 2F4



Their structures are almost identical except for the insertion of an ether oxygen between the third and fourth carbon atoms of the side chain. Poly-FBA (1F4) was developed first and 2F4, the improved modification. Typical vulcanization formulation for the two rubbers and their properties are shown in Table XVII. The properties of a high acrylonitrile content nitrile rubber (NBR), based on typical sulfur cure is included for comparison.

The elastomer 1F4 is much superior to NBR in resistance to hydrocarbon fuels. The distinct advantage of 2F4 over 1F4 is the much improved behavior at subzero temperatures. In addition it is slightly more solvent resistant than 1F4. Low volume increases of 2F4 were observed even in those solvents which swelled 1F4 to a high degree.

Most of the compounding studies^{83, 92} and data were on 1F4 since it was the first fluoroacrylate elastomer developed. Hamlin⁹² reported that 1F4 possessed good resistance to various hydrocarbon fuels and solvents; however, its most valuable characteristic was the resistance to synthetic diester-type lubricants, even at high temperatures. This is shown in the retention of tensile strength after exposure to this lubricant, Table XVIII.

Landrum⁶⁷ reported that nitrile rubber (NBR) was brittle after 500 hours in diester fluid at 350° F (177° C). Testroet⁹³ determined the effect of aromatic fuels on elastomeric vulcanizates, including several fluorine-containing rubbers.

TABLE XVIII

RESISTANCE OF 1F4 TO DIESTER LUBRICANT AT 350° F
(MIL-L-7808 Jet Engine Oil)

Original tensile strength, psi	1300
Tensile strength after 250 hrs, psi	1080
Tensile strength after 500 hrs, psi	1020
Tensile strength after 1000 hrs, psi	870

TABLE XIX
VOLUME INCREASE IN PER CENT AFTER IMMERSION IN
70:30 ISOCTANE-TOLUENE AT 25° F

	70 hrs	7 days
1F4 (Poly FBA)	27	27
Kel-F Elastomer 3700	14	17
Viton A	2	3
Fluorinated silicone (LS-53)	22	22
Polyfluoroester* (Hooker)	19	

* 24 hours instead of 70 hours, from Rept #6, QM R&E Command⁴⁴.

It is interesting to note the volume increase of 1F4 as compared with other fluoroelastomers, Table XIX.

The resistance of 1F4 to aromatic fuels is essentially similar to fluoropolyester and LS-53; however, it is inferior to that of the vinylidene fluoride copolymers, Kel-F Elastomer 3700 and Viton A or Fluorel. The development of these two types of elastomers has markedly limited the applications of the fluoroacrylate polymers.

D. FLUOROPOLYESTERS

Another approach to the development of a chemical-resistant low-temperature elastomer was the polycondensation of fluorine-containing intermediates. This phase of research was started by Hooker Chemical Company under Air Force sponsorship. The high molecular weight polyesters were prepared from the reactions of glycols⁹⁶ with dicarboxylic acids, dicarboxylic acid chlorides or diethyl esters. Fluorine-containing polyamides were also prepared by reaction of diesters, such as diethyl perfluoroglutarate and a hydrocarbon diamine, such as bis-(N-ethyl)-1,6-hexanediamine.

The most promising fluorine-containing elastomer developed under this project was the hexafluoropentylene adipate polyester⁹⁶. The rubber could be vulcanized by dicumyl peroxide and reinforced with carbon black. Landrum⁴⁴ has used, in addition, ultrafine precipitated calcium carbonate. Some of the properties of the vulcanizate, taken from Wilson's⁹⁴ results, are shown in Table XX.

At first glance, the Gehman values and the brittle point would indicate superior low-temperature flexibility. However, this was negated by the tem-

TABLE XX
PROPERTIES OF THE FLUOROPOLYESTER

Tensile strength, psi	2100
Elongation, %	270
Hardness, Shore A	56
Low temperature characteristics:	
Torsional, Gehman, ° C	T ₂ —minus 30
	T ₅ —minus 47
	T ₁₀ —minus 51
Temperature retraction, ° C	
	TR10—minus 39
	TR30—plus 3
	TR50—plus 6
	TR70—plus 10
Brittle point, ° C	—minus 73

perature retraction, TR, properties of the elastomer. The TR values showed that the elastomer, if held at low temperatures in a stretched condition, would lose its elasticity or "rubbery" properties due to crystallization. Bartholomew³ and others also reported the crystallization of the fluoropolyester at moderately low temperatures. Additional tests at the QMC laboratory showed that samples of the vulcanizate held for 3 days at minus 30° F were approximately 25 times stiffer than those held for 10 minutes at the same temperature. The TR test also indicated once elasticity is lost due to stretched exposure at low temperatures, that elasticity was not regained until the vulcanizate was heated to approximately 40° F.

The fluorinated polyester elastomer possesses good fuel and solvent resistance at elevated temperatures. Postelnek⁹⁷ stated that when carbon black alone was used as filler, good oil aging was observed and the use of calcium carbonate resulted in good air aging. Griffin⁹⁸ obtained 31% volume increase and 65% tensile strength retention after immersion of the vulcanizate in 70:30 isooctane-toluene for 70 hours; and 4% volume increase and 85% tensile strength retention after immersion in JP-5 under the same conditions of time and temperature. The volume increase, after 24 hours in boiling water was only 1% and a loss of only 14% of the original tensile strength. The combination of solvent resistance and low temperature flexibility was better than that of the commonly used NBR rubbers. The superiority was due mainly to good solvent resistance. The low temperature limit of its serviceability was in approximately the same temperature range as for the nitrile rubbers. One serious disadvantage of the fluoropolyester elastomer, however, was the high degree of crystallization at low temperatures resulting in high compression set and loss of rubberiness.

A modified polyester, the hexafluoropentylene adipate-isophthlate was reported by Wilson⁹⁹ to be superior in solvent and chemical resistance to the original polyfluoroester elastomer, but inferior in low temperature characteristics.

E. FLUORINATED SILICONE ELASTOMER

The early researches of Van Helmont, Berzelius, Crafts, Wohler, Friedel and particularly Kipping on organo-silicones are well known. Dumas⁹⁰ as early as 1840, predicted that the carbon atom in the hydrocarbons could be replaced by other elements such as those under Group IV of the Periodic Table. Silicone belongs to this group. The development of silicone rubbers is closely identified with works of Rochow¹⁰⁰, Post¹⁰¹ and the industrial companies of Dow Corning Corporation, General Electric Company and Union Carbide Corporation.

Silicone rubbers have the distinct reputation for retention of physical properties over the widest range of temperatures (minus 100° F to plus 600° F). It is, therefore, a logical step to incorporate the necessary chemical resistance into the silicones with the hope that their original low and high temperature characteristics could be retained. Two of the methods attempted were the development of silicone polysulfide¹⁰² and fluorinated silicone¹⁰³ rubbers. The latter was more successful.

The early work of McBee and Pierce¹⁰⁴, in cooperation with the Air Force, led the way for the synthesis of fluoroalkyl silicone monomers. Subsequently, Tarrant, Dyckes and Wise¹⁰⁵ synthesized, among others, the trifluoropropyl methylchlorosilane monomer which would be readily converted into the cyclic trimer and tetramer. The Dow Corning Corporation, under a cooperative

TABLE XXI
PROPERTIES OF FLUROSILICONE RUBBER, LS-53

Tensile strength, psi		1000
Elongation, %		200
Hardness, Shore A		60
Low temperature characteristics:		
Gehman torsional, °C	T ₂	-51.3
	T ₅	-56.3
	T ₁₀	-60.4
Temp.-retraction, °C	TR10	-66.7
	TR30	-60.3
	TR50	-54.3
	TR70	-48.5
Compression set, %		
After 4 days at	-40° F	-65° F
10 sec reading	52.4	95.2
30 min reading	23.6	88.9

program with the Air Force, was successful in polymerizing the fluoroalkyl silane. The homopolymer of trifluoropropyl methyldichlorosilane, known as Silastic LS-53, is currently produced commercially by Dow Corning Corporation. The backbone of the molecular chain of the polymer is still a siloxane unit and the fluorine atoms are in the pendant position. Polmanteer and Hunter¹⁰⁶ recently discussed the relationship of polymer composition and low temperature characteristics of polysiloxane elastomers. Haszeldine, Newlands and Plumb¹⁰⁷ are currently investigating the chemistry of fluoroalkyl polysiloxanes, with particular emphasis on the effect of the position of the fluorine atoms within the molecule.

Silastic LS-53 possesses a good combination of low temperature flexibility, chemical resistance and stability at high temperatures. Its tensile strength is inferior to those of nitrile rubber, SBR and neoprene, although it compares favorably with other silicone rubbers. The original physical properties of LS-53¹⁰⁸ and its behavior at subzero temperatures are shown in Table XXI. Table XXII, taken from data by Dellaria¹⁰⁹, shows the resistance of LS-53 to fuels, solvents and hydraulic fluids at various temperatures. Talcott, Brown and Holbrook¹¹⁰ obtained similar results.

TABLE XXII
VOLUME INCREASE OF FLUROSILICONE RUBBER AFTER
IMMERSION IN LIQUIDS

Liquids	Immersion time & temp.	Volume increase, %
70:30 isooctane-toluene	3 days @ 158° F	18
JP-4	14 days @ 250° F	18
JP-5	7 days @ 75° F	4
Silicate ester*	3 days @ 350° F	6
Hydraulic fluid**	3 days @ 350° F	9
Skydrol 500	3 days @ 212° F	28
Kylene	7 days @ 75° F	19
Carbon tetrachloride	7 days @ 75° F	21

* Oronite 8200.

** Oronite 8515.

The low temperature flexibility of LS-53 is not as good as the ordinary silicone rubbers; however, it is better than any chemical and fuel resistant elastomers currently available. The fuel resistance is superior to nitrile and neoprene rubbers, but inferior to Fluorel or Viton A. Another outstanding property of LS-53 is heat stability. It was found that after 52 weeks of heat aging at 392° F, the rubber still retained approximately 35% of its original tensile strength. Servais and Polmanteer¹¹ reported that aging LS-53 for 16 weeks at 400° F reduced the tensile strength and elongation only 40% and the durometer hardness only a few points.

Dow Corning Corporation has placed on the market a modified fluorosilicone rubber known as Silastic LS-63. It was designed for easier handling and processing in extruders, calenders and rubber mills. It blends readily with other types of silicone rubbers and can be colored to any desired shade.

F. FLUOROPOLYAMIDINE

Although this experimental polymer has not been produced in any appreciable amount nor has it undergone regular vulcanization, it is mentioned here briefly due to its unusual stability at high temperatures. Brown¹¹² at the University of Florida, under a research project supported jointly by the Wright Air Development Division and the Office of Naval Research, first obtained the polymer by the pyrolytic condensation of a perfluoromonoamidine and perfluorodiamidine with the formation of a triazine nucleus. The product varied from the soft elastomeric solids to brittle resins. The elastomeric material has interesting properties. It was heated in air at 570° F for prolonged period of time with no apparent change; however, after 30 minutes exposure to 937° F (475° C), it lost 50% of its weight, although it still retained the rubbery properties¹¹³.

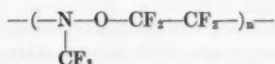
The primary deficiency of the elastomer, according to Gibbs¹¹⁴ and Bartholomew³, was the highly crosslinked nature of the gum, thereby rendering it unsuitable for most applications. Polymerization by melt and solution reactions using ionic and free-radical initiators¹¹⁵ also resulted in crosslinked products. Research is continuing to eliminate or minimize this deficiency. Brown^{116, 117} reported the progress of his investigations on difunctional monomers, including the reaction of the fluorinated dinitriles with the amidines, to produce linear polyfluoroamidines.

G. FLUORINATED NITROSO ELASTOMERS

Several rubber reviews¹¹⁸ which were published under different categories, such as "high temperature elastomeric compounds"¹¹⁹ and "rubbers for special service conditions"¹⁷² have included the various types of fluorine-containing elastomers. However, the nitroso-type rubbers due to their recent development, were not described in these reviews. The nitroso rubbers, therefore, will be discussed more fully to cover monomer synthesis, polymerization, vulcanization and properties. The elastomer program of the QMC during the past few years has placed major emphasis on fluorinated nitroso derivatives. A family of nitroso elastomers is being developed through the cooperative team effort of universities, industry and government laboratories. This is a continuation of the research on fluorine initiated by the QMC in 1950.

1. *Trifluoronitrosomethane-tetrafluoroethylene copolymer*.—The first elastomer developed was an equimolar copolymer of trifluoronitrosomethane (CF_3NO) and tetrafluoroethylene (C_2F_4). Since this copolymer has been studied more

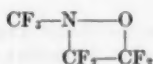
than the others, from monomer synthesis and polymerization to vulcanization (though far from complete), most of the description and discussion will be focused on this nitroso rubber. The molecular structure of the repeating unit of the polymer is represented by



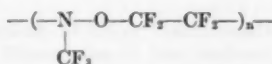
a. Monomer synthesis.—Trifluoronitrosomethane, CF_3NO , is a deep blue gas with a boiling point of minus 84°C . It was first prepared by Ruff and Giese¹¹⁹ by the fluorination of silver cyanide in the presence of silver nitrate. It was claimed that the oxygen probably came from the impurities of the reactions. Barr and Haszeldine¹²⁰ synthesized it by the reaction of trifluoriodomethane (CF_3I) and nitric oxide (NO) in the presence of ultraviolet light and with mercury as catalyst. Some experiments have been made by Tarrant¹²¹ and others in which it was found that strong sunlight gave better conversion and shorter reaction time than by irradiation with an ultraviolet lamp. The progress of this reaction can be followed readily, since the mixture of CF_3I and NO is brown in color and when the mixture turns blue, the reaction can be considered complete. Crawford, Rice and Montermoso^{122,123} reported the use of trifluorobromomethane (CF_3Br) in lieu of CF_3I . CF_3Br is comparatively inexpensive and is readily available commercially.

The other comonomer, tetrafluoroethylene (C_2F_4) is commercially available. The du Pont Company is the major producer; its homopolymer is known as Teflon. As early as 1890 several papers¹²⁴⁻¹²⁶ were published describing attempts to prepare C_2F_4 by the reactions of fluorine with carbon or with chloromethanes and also of silver fluoride with tetrachloroethylene. The basic chemical reactions in the commercial synthesis of C_2F_4 are (1) reaction of fluorspar (CaF_2) and sulfuric acid to produce HF , (2) reaction of HF with chloroform to give chlorodifluoromethane, CHClF_2 , and (3) pyrolysis of CHClF_2 to gaseous C_2F_4 . The homopolymerization of C_2F_4 to Teflon has been discussed earlier.

b. Polymerization.—The elastomer is a 1:1 mole copolymer of CF_3NO and C_2F_4 . Barr and Haszeldine¹²⁰ found that CF_3NO reacted slowly with C_2F_4 in the dark at room temperature giving rise to 30 to 65% of a colorless gas, b.p. -6.8°C of empirical formula $\text{C}_3\text{F}_7\text{NO}$, and they identified it as oxazetidine, a cyclic adduct. Another product amounted 35 to 70% of an almost colorless viscous oil, described as polymeric and of the same empirical formula. The molecular structures of these products are as shown



Oxazetidine



Polymeric oil

The ratio of the gaseous product to the polymeric oil could be controlled by reaction temperature; the higher temperatures favored the gas formation. An ionic mechanism was proposed for the reaction. Later, these same workers¹²⁷ suggested the alternative possibility of a gas-phase, radical-type mechanism for the formation of polymer, oxazetidine, or both. Crawford¹²² and others, on the other hand, presented experimental data which appear both to preclude an

ionic polymerization and heavily support a free radical mechanism. Preliminary kinetic data¹²³ was later presented. Recently, Crawford, Rice and Landrum¹²⁸ discussed the polymerization mechanism for formation of fluorinated nitroso elastomers and summarized the evidence supporting the free radical type of reaction.

In 1957, Minnesota Mining and Manufacturing Company and the Quartermaster Corps were already engaged in incorporating heteroatoms in the backbone of the polymer molecules as a means of improving the low temperature flexibility of fluorine-containing, elastomers. Among the many approaches, the nitroso derivative was explored, theorizing that the reported oil (m.w.—7000)



FIG. 1.—Showing nonflammability characteristic of $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ elastomer. (From QMC Rubber Research reports.)

by Barr and Haszeldine¹²⁰ would be elastomeric at molecular weights of 100,000 or above. Crawford and Montermoso¹²⁹ reported in 1958 that an elastomeric copolymer of CF_3NO and C_2F_4 was obtained by bulk polymerization with the exclusion of air, moisture, or light.

It was found that the elastomer may be made in any of three methods: bulk, solvent and water emulsion polymerizations. The water emulsion method is the most desirable due to simpler control of reactions and to practical economy for potential large volume production; however, bulk polymerization has been found to produce the elastomer with higher molecular weight. The inherent viscosities of the materials obtained by this method which was carried out at minus 20° C, ranged from 0.6 to 0.85, indicating a significant increase over the

values obtained previously (0.15 to 0.3) by the water emulsion method. The solvent polymerization did not produce polymer with as high molecular weights as did the bulk method.

The laboratory procedure for the bulk polymerization as described by Crawford¹²² and others was essentially as follows: the monomers CF_3NO and C_2F_4 in equimolar amounts were condensed in pyrex ampoules, sealed and allowed to warm to the desired polymerization temperature. The progress of the reaction was indicated by the disappearance of the characteristic blue color of CF_3NO in the reaction mixture. The unreacted monomers were then removed by flashing under vacuum. The polymer was removed by dissolving it in trichlorotrifluoroethane (Freon 113) and the per cent yields, conversions and properties determined. Efforts are in progress on finding better, cheaper and

FLUORINE-CONTAINING RUBBERS
LOW TEMPERATURE SERVICE PROGRESS

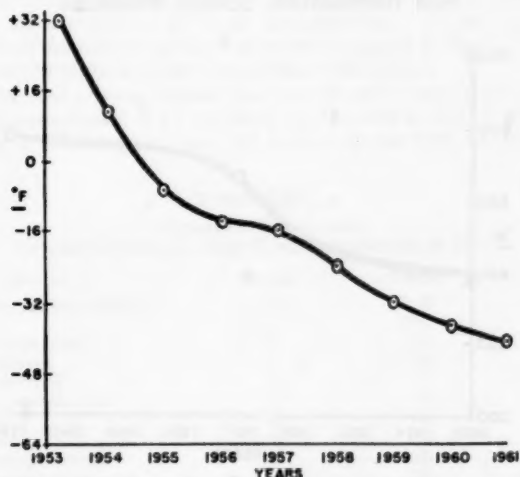


FIG. 2.—Showing progress in the development of chemical-resistant fluorine containing elastomers for use under sub-zero temperatures. (From QMC Rubber Research reports.)

more practical methods. Recently, a modified water suspension polymerization offers potential promise. A great deal of investigations needs to be done to improve polymerization methods and techniques.

c. Vulcanization and properties.—The properties of the unvulcanized copolymer of CF_3NO and C_2F_4 have been described in several papers¹²⁰⁻¹²². The unvulcanized gum is a clear transparent rubber which has been found to be completely nonflammable. When a piece of the gum was directly exposed to a flame of a bunsen burner, for example, some gas was evolved which tended to put out the flame, see Figure 1. This is probably the first rubber known that would not flame. Polychloroprene (neoprene), although possessing self-extinguishing properties, burns when exposed to direct flame. The molecular weight, determined by light scattering technique is over one million. Its glass

transition temperature is minus 51° C. The volume increase after immersion for 24 hours at 25° C in 70:30 isooctane-toluene mixture is only 3%. It is totally insoluble in acetone, methylethyl ketone, tetrahydrofuran and other solvents except to those containing fluorine such as the Freons. It was also found to possess unusual resistance to chlorine trifluoride. The weight loss after 20 hours in an oven at 200° C (392° F) is negligible. Thus, the elastomer has a good combination of inherent properties not present in any other rubber.

The most effective vulcanizing system, to date, for the $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ copolymer is a combination of triethylene tetramine (TETA) and hexamethylene diamine carbamate (HMDA-C). The gum vulcanizate of the nitroso rubber, however, has a tensile strength of less than 300 pounds per square inch. A variety of reinforcing fillers were investigated to improve the tensile strength. The carbon black fillers caused sponging with the amine cures, regardless of the

FLUORINE-CONTAINING RUBBERS HIGH TEMPERATURE SERVICE PROGRESS

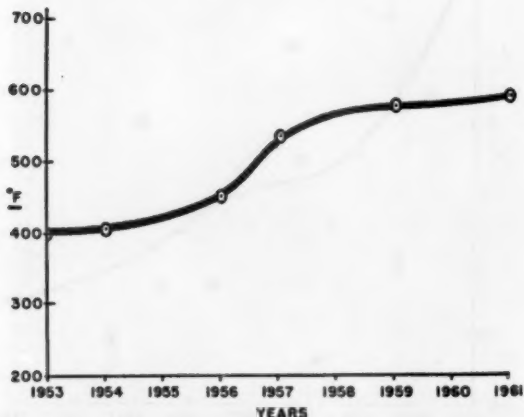


Fig. 3.—Showing progress made in the development of chemical-resistant fluorine-containing elastomers for use under extremely high temperatures. (From QMC Rubber Research reports.)

type and acidity (pH) of the blacks and of the temperature of vulcanization. Fine particle silicon oxides, such as the Hi-Sils, were the most effective reinforcing fillers. The physical properties were found to depend on the molecular weight of the polymers. Table XXIII shows the compound formulation and physical properties at 25°C.

The chemical resistance and low temperature characteristics of the nitroso elastomer were determined and compared with those of two commercially available rubbers, Fluorel and Hycar 1001 (NBR). These are shown in Tables XXIV and XXV.

Table XXIV indicated the superior chemical and solvent resistance of the nitroso elastomer. Even after immersion in red fuming nitric acid, RFNA, for 48 hours, it swelled only 28% compared to 70% for Fluorel, a copolymer of perfluoropropylene and vinylidene fluoride. It was also found that the effect

TABLE XXIII
FORMULATION AND PHYSICAL PROPERTIES AT 25° C

CF ₃ NO—C ₂ F ₄ copolymer	100			
SiO ₂ (HiSil 303)	15			
TETA	1.25			
HMDA-C	2.50			
Press cure: 60 min at 250° C				
Post oven cure: 18 hrs at 212° C				
M.W. × 10 ⁴	.4	.6	.81	1.14
Tensile strength, psi	300	470	700	1100
Elongation, %	540	520	600	420
Hardness, Shore A	65	55	55	66

of red fuming nitric acid on the nitroso rubber has reached equilibrium after 24 hours. In another set of measurements, the volume increase after 24 hours immersion in RFNA was 25.2% and after 7 days, 25.5%.

The nitroso rubber, with Gehman T₅ of minus 41° C and TR30 of minus 40° C would be serviceable at those temperatures. It can be seen from Table XXV that the nitroso rubber has an advantage of at least 25° C over the Fluorel and nitrile rubbers in low temperature flexibility.

In addition, the nitroso rubber has been found to be ozone and sunlight resistant. It was exposed in an ozonator for 24 hours at 150° F with an ozone concentration of 17,500 parts per 100 million in air without cracking. No

TABLE XXIV
CHEMICAL RESISTANCE
Volume increase, %, after 48 hours immersion at 25° C

Solvent	Nitroso	Fluorel	Nitrile
70:30 Isooctane-toluene	2	3	24
Acetone	2	188	147
Acetic anhydride	3	161	108
Benzaldehyde	1	75	259
Benzyl alcohol	1	1	179
Carbon tetrachloride	5	4	50
Ethylether	2	59	21
Formaldehyde	3	3	3
Methylethyl ketone	2	199	175
Red fuming nitric acid	28	70	decompose

TABLE XXV
LOW TEMPERATURE FLEXIBILITY
Gehman Relative Torsional Modulus, ° C

	Nitroso	Fluorel	Nitrile
T ₂	-31	-10	-7
T ₄	-41	-13	-13
T ₁₀	-44	-14	-14
T ₁₀₀	-47	-21	-18
Temperature Retraction, ° C			
TR70	-29	-9	-9
TR50	-36	-13	-12
TR30	-40	-16	-14
TR10	-46	-19	-18

visible cracks were observed after roof exposure for 2 months at 20% elongation. Although not as thermally stable as Viton A or Fluorel, its stability is better than most commercial rubbers. The weight loss of the raw gum was negligible after 20 hours in an oven at 200° C (392° F).

2. *Other nitroso copolymers.*—A large family of nitroso copolymers is being prepared. This can be achieved both by varying the structure of the nitroso monomer or by varying the comonomer. Two nitroso monomers of particular interest from the standpoint of their availability and properties of the copolymers formed are: 1-nitroso-2-nitrotetrafluoroethane ($\text{ONCF}_2\text{CF}_2\text{NO}_2$) and 1-nitroso-2-chlorotetrafluoroethane ($\text{ONCF}_2\text{CF}_2\text{Cl}$). Both copolymerize readily with C_2F_4 . The properties of the copolymers are similar to those of the $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ copolymer. Detailed investigations, however, are very preliminary and further discussion would be premature. The molecular structure of the copolymers may be represented:

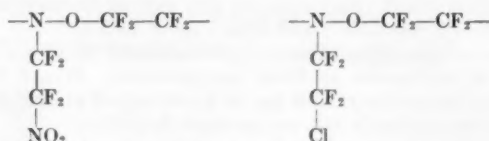


Table XXVI indicates the copolymer systems other than $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ and the results obtained thus far.

TABLE XXVI
COPOLYMER SYSTEMS OTHER THAN $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$

Comonomer	Time, hrs	Temp. °C	Conversion	Polymer
Copolymers of C_2F_4				
$\text{C}_2\text{F}_5\text{NO}$	24	-16	Quant.	rubbery
$\text{C}_3\text{F}_7\text{NO}$	24	-20	Quant.	rubbery
$\text{C}_6\text{F}_{17}\text{NO}$	24	-20	50%	rubbery
$\text{HC}_2\text{F}_3\text{NO}$	24	-50 to -20	90%	rubbery
Copolymers of CF_3NO				
CF_2CFH	6	-20	85%	elastomeric
CF_2CFCI	24	-15	Quant.	elastomeric
CF_2CFCF_2	11 weeks	-20	20%	elastomeric
CF_2CH_2	3 weeks	-15 to -20	37%	grease
CFHCH_2	48	-16 to -20	0	—
CH_2CH_2	3 weeks	-16 to -20	0	—
CF_2CCl_2	24	-20	Quant.	tough elastic
$\text{CFCICF}-\text{O}-\text{CH}_3$	12	-15	Quant.	plastic
Styrene	24	-14	—	oil
Butyl methacrylate	24	-14	80%	oil
Copolymers of $\text{ONCF}_2\text{CF}_2\text{NO}$				
CF_2CF_2	24	-25	90%	elastomeric
CF_2CFCI	24	-25	92%	brittle plastic
CF_2CFH	24	-25	80%	stiff gum
$\text{CF}_2\text{CH}_2\text{OCHCH}_2$	24	-25	98	brown oil
Copolymers of ONCF_2Cl				
CF_2CF_2	8 days	-65 to -35	82%	elastomeric
CF_2CFCI	20	-20	—	short elastic
CF_2CH_2	20	-20	—	plastic

The current work on nitroso derivatives has opened up a broad and promising field for investigations. The new monomers used in the copolymerizations have been described by Crawford¹³², Park¹³⁴, Tarrant¹³⁵, Stefani¹³⁶ and others in various publications and technical papers.

VI. DISCUSSION

At the early stage of the Arctic Rubber Program, which started in 1948, the author was asked what kind of ideal rubber was the QMC looking for. Without hesitation he said that QMC would settle for a rubber possessing the strength of natural rubber, the low temperature flexibility of silicone and the chemical resistance of Thiokol. We have not obtained this rubber yet but we are certainly getting close to it. What makes the current objective more difficult to meet is the addition of new requirements resulting from the development of modern weapons. However, it is not actually expected that any single rubber will solve all the problems.

In the search for elastomers possessing a combination or combinations of desirable qualities, it is felt that the area of fluorine-containing compounds was a wise choice to investigate. Significant progress has been made since 1950. Literally, thousands of new rubbers have been prepared, in gram quantities. After screening, only a small fraction of about 1% were selected for more detailed evaluation. Even then, there was no assurance that they will be commercially produced.

Not all the elastomers presented and discussed in this review reached commercial production. Polyfluoroprene occupied a position, as far as properties are concerned, between neoprene and polybutadiene. In addition, to produce polyfluoroprene would cost more than neoprene or polybutadiene. Hence, its production was discontinued. The trifluorobutadiene rubber was equal to neoprene in low temperature flexibility, but better in chemical resistance. Compared to nitrile rubber, the polytrifluorobutadiene was equal in chemical resistance, but better in low temperature flexibility. Here was a rubber that was better than both neoprene and nitrile rubber but did not reach the open market for economic reasons. The cost of producing this rubber would be prohibitive and noncompetitive with either neoprene or nitrile rubber. Besides, there were some rubbers commercially available that possessed better low temperature flexibility and others with superior chemical resistance. Polyfluoroester was not produced in larger quantities for similar considerations. The Vitons and Fluorel, Kel-F Elastomers and fluorinated silicone are commercially available. The fluoroacrylate elastomer, 1F4, is being produced commercially but its use has been limited since the development of vinylidene fluoride copolymers. The fluorinated nitroso rubbers are still in the experimental or laboratory stage, although larger production is being contemplated.

From the data presented, the fluorinated silicone, LS-53, has the best low temperature flexibility, followed by the nitroso rubber. In chemical resistance, the nitroso rubber comes first, followed by Viton or Fluorel, and the Kel-F Elastomers. The most comprehensive comparative study of high temperature stability of various rubbers, was made by Bergstrom¹³⁷. The nitroso rubber was not available for this study. He determined the temperature at which the vulcanizate retained 75% of the original tensile strength after aging for 8 hours. The tensile strength was measured at room temperature. The results obtained were in this order: Viton A@530° F; Kel-F Elastomer 3700@450° F; LS-53@430° F; and Poly FBA@370° F. When the tensile strength was

determined at high temperatures, these rubbers retained 50% of their original tensile strength at 170 to 190° F. In flame retardance or nonflammability, the nitroso rubber is outstanding, followed by Viton A or Fluorel, Kel-F Elastomers, LS-53 and 1F4. The nitroso rubber is the only elastomer known that would not flame. A deficiency of LS-53, 1F4 and the still experimental nitroso rubber is their low tensile strengths which are less than 1500 psi. Viton A, Fluorel and the Kel-F Elastomers have tensile strength over 2000 psi. All these fluorinated rubbers are expected to be resistant to ozone, weather and radiation since they are all saturated and contain fluorine in their molecule.

The steady progress made in the development of chemical-resistant fluorine-containing elastomers for use under extremely low and extremely high temperatures is graphically shown in Figures 2 and 3 respectively.

With the rapid continuous advances in travel, particularly in the fields of rockets, jets, missiles and nuclear submarines as well as in civilian transportation, the functional demands on elastomers will continue to increase. It is believed that the fluorine-containing elastomers, including those which may be developed in the future, will play an important role in meeting these requirements.

VII. ACKNOWLEDGMENT

A scientific review of this kind cannot be made without the considerable assistance of those associated with the particular field. The author would like to express his appreciation to the researchers and authors of technical papers surveyed in this review for their valuable contributions. Particular acknowledgement is made to his close associates, Drs. J. Copenhaver, B. F. Landrum and G. H. Crawford of Minnesota Mining and Manufacturing Company; Drs. P. Tarrant and J. D. Park of Florida and Colorado Universities respectively; Mr. C. B. Griffis, Mr. A. Wilson and Dr. G. R. Thomas of the QMC Laboratories. Appreciation is also expressed to Dr. G. E. P. Smith, Jr. and Dr. B. L. Johnson of Firestone Chemical and Physical Research Laboratories and to Dr. D. Craig of the B. F. Goodrich Research Center for reviewing the manuscript and for their valuable suggestions.

VIII. REFERENCES

- 1 Mochel, W. E. and others, *Ind. Eng. Chem.* **40**, 2285 (1948).
- 2 Operations Frost, Frigid and Williaw, AGF Reports (1947).
- 3 Bartholomew, E. R., Eykamp, G. R. and Gibbs, W. E., *RUBBER CHEM. AND TECHNOL.*, **32**, No. 5, 1587 (1959).
- 4 Monterosso, J. C., QM Rubber Program Report (1955).
- 5 QMC Project "Thermal Protection of the Individual Soldier", (1956).
- 6 Moissan, H., *Compt. rend.* **102**, 1543; **103**, 202, 256 (1886).
- 7 Pinkston, J. J., Jr., *Ind. Eng. Chem.* **39**, 255 (1947).
- 8 Pauling, L., "Nature of the Chemical Bond", Cornell Univ. Press (1939).
- 9 Cottrell, T. L., "The Strengths of Chemical Bonds", Academic Press, Inc. (1954).
- 10 Renfrew, M. M. and Lewis, E. E., *Ind. Eng. Chem.* **38**, 870 (1946).
- 11 Brockway, L. O., *J. Phys. Chem.*, **41**, 185 (1937).
- 12 Rudner, M. A., "Fluorocarbons", Reinhold Pub. Corp. (1958).
- 13 Brewster, R. Q. and McEwen, W. E., "Organic Chemistry," 3rd ed., Prentice Hall, Inc., (1961).
- 14 Plunkett, R. J., U. S. Patent 2,230,654 (1941).
- 15 Brubaker, M. M., U. S. Patent 2,393,967 (1946).
- 16 Joyce, R. M., Jr., U. S. Patent 2,394,243 (1946).
- 17 Dolan, R. C. and others, Paper presented before 130th ACS Meeting (1956).
- 18 I. G. Farbenindustrie, British Patent 465,520 (1937).
- 19 Kropa, E. L., and Padbury, J. J., U. S. Patent 2,531,134 (1950).
- 20 Dittman, Passino and Wrightson, U. S. Patent 2,689,241.
- 21 Buts, L. W., Paper presented at JANA Conf. on Elastomer R&D (1958).
- 22 Lovelace, A. M., Postelnik, W. and Rausch, D. A., "Aliphatic Fluorine Compounds, ACS Monograph No. 138", Reinhold Pub. Co. (1958).
- 23 Coffman, D. D. and Salisbury, L. F., U. S. Patent 2,451,612 (1948).
- 24 Imperial Chem. Ind. Brit. Patent 603,855 (1948).
- 25 Johnson, F. W., U. S. Patent 2,398,181 (1946).

- ²² Salisbury, L. F., U. S. Patent 2,426,792 (1947).
- ²³ Salisbury, L. F., U. S. Patent 2,437,307 (1948).
- ²⁴ Salisbury, L. F., U. S. Patent 2,469,948 (1949).
- ²⁵ Salisbury, L. F., U. S. Patent 2,519,199 (1950).
- ²⁶ Nieuwland, J. A. and others, *J. Am. Chem. Soc.* **53**, 4197 (1931).
- ²⁷ Hill, F. B., U. S. Patent 2,436,213 (1948).
- ²⁸ Hill, F. B., Canadian Patent 459,661 (1949).
- ²⁹ Imperial Chem. Industries, British Patent 591,086 (1947).
- ³⁰ Mochel, W. E., U. S. Patent 2,426,560 (1947).
- ³¹ Mochel, W. E., Canadian Patent 459,955 (1949).
- ³² Starkweather and others, *Ind. Eng. Chem.* **39**, 210 (1947).
- ³³ Orr, R. J. and Williams, H. L., *Can. Jour. Chem.* **33**, 1328 (1955).
- ³⁴ Mochel, W. E. and Hall, M. B., *J. Am. Chem. Soc.* **71**, 4092 (1949).
- ³⁵ Vanderbilt Rubber Handbook, p. 238 (1958).
- ³⁶ Wilson, A., Griffin, C. B. and Montermoso, J. C., *Rubber World*, **139**, 68 (1958).
- ³⁷ ASTM Designation: D 1329-58T, Rubber Products, 19th Edition (1960).
- ³⁸ Gilbert, R. D. and Williams, H. L., *J. Am. Chem. Soc.* **74**, 4114 (1952).
- ³⁹ Hoyt, J. M., U. S. Patent 2,843,575 (1948).
- ⁴⁰ Landrum, B. F., Paper Presented to Plastics & Rubber Meeting, Society of German Chemists, Bad Nauheim, Germany (1960).
- ⁴¹ Tarrant, P. and others, QMC Prog. Repts. Cont. DA19-129-QM-500.
- ⁴² Copenhaver, J. and others, QMC Prog. Repts. Cont. DA19-129-QM-1043.
- ⁴³ Montermoso, J. C. and Griffin, C. B., Paper presented at JANA Conf. on Elastomer R&D (1956).
- ⁴⁴ Unpublished Data, QM Res. & Engr. Command.
- ⁴⁵ Swarts, F., *Bull. Acad. Roy. Belg.* **1901**, 383 (1919).
- ⁴⁶ McBee, E. T., Hill, H. M. and Bechman, G. B., *Ind. Eng. Chem.* **41**, 70 (1949).
- ⁴⁷ Gilman, H. and Hones, R. G., *J. Am. Chem. Soc.* **65**, 2037 (1943).
- ⁴⁸ Swarts, F., *Bull. Soc. Chem.* **25**, 145 (1919).
- ⁴⁹ Robb, L. E., Honn, F. J. and Wolf, D. R., Paper presented at Joint Meeting of the Rubber Div., ACS and Canadian Chem. Inst. (1957).
- ⁵⁰ Griffin, C. B. and Montermoso, J. C., *Rubber Age* **77**, 559 (1955).
- ⁵¹ Jackson, W. W. and Hale, D., *Rubber Age* **77**, 865 (1955).
- ⁵² Montermoso, J. C. and others, *Proc. Inst. Rubber Industry*, **5**, 97 (1958).
- ⁵³ Conroy, M. E. and others, *Rubber Age* **76**, 543 (1955).
- ⁵⁴ Headrich, R. E., WADC Tech. Rept. 55-377 (1955).
- ⁵⁵ Smith, L. C. and others, WADC Tech. Rept. 55-492 (1957).
- ⁵⁶ Bolstad, A. N., Prog. Rept. RL 55-401, M. W. Kellogg Co. to QMC (1955).
- ⁵⁷ Conroy, M. E. and others, Paper presented at Meeting of Rubber Div., ACS (1954).
- ⁵⁸ Robb, L. E. and others, Paper presented at Meeting of Rubber Div. ACS (1954).
- ⁵⁹ Honn, F. J., *Rubber World* **135**, 891 (1957).
- ⁶⁰ Dixon, S. and Rexford, D. R., Paper presented at Fluorine Chem. Symposium, ACS, (1956).
- ⁶¹ Adams, R. M., and Bovey, F. A., *J. Polymer Sci.*, **9**, 481 (1952).
- ⁶² Bolstad, A. N., Lo, E. S., and Benning, C. J., M. W. Kellogg, Rep. to QMC under Cont. DA19-129-QM 1580 (1956).
- ⁶³ Landrum, B. F., Paper presented at the Army Conference on Elastomers, QMR&E Command, Natick, Mass., October 1955.
- ⁶⁴ Lo, E. S., Crawford, G. H. and Landrum, B. F., M. W. Kellogg Co. Rept. to QMC under Cont. DA19-129-QM 1580 (1955).
- ⁶⁵ Bolstad, A. N., M. W. Kellogg Co. Rept. to QMC under Cont. DA19-129-QM-1580 (1955).
- ⁶⁶ Wilson, A., Griffin, C. B. and Montermoso, J. C., CP-4, QMR&E Command (1957).
- ⁶⁷ Wilson, A., Griffin, C. B. and Montermoso, J. C., *Rubber Age* **83**, 647 (1958).
- ⁶⁸ Bovey, F. A., from a chapter in "Modern Materials", Academic Press, Inc. (1958).
- ⁶⁹ Stivers, D. A., Honn, F. J. and Robb, L. E., *Ind. Eng. Chem.* **51**, 1465 (1959).
- ⁷⁰ Stivers, D. A., Peterson, D. L. and Meier, G. R., *Rubber Age* **88**, 292 (1960).
- ⁷¹ Dixon, S., Rexford, D. R. and Rugg, J. S., *Ind. Eng. Chem.* **49**, 1687 (1957).
- ⁷² Griffin, W. R., WADC Tech. Rept. 57-475 (1957).
- ⁷³ Rugg, J. S. and Stevenson, A. C., *Rubber Age* **82**, 10 (1957).
- ⁷⁴ Kelble, J. M., Paper presented at JANA Conf. on Elastomer R&D (1958).
- ⁷⁵ Moran, A. L., *Rubber World* **137**, 250 (1957).
- ⁷⁶ Moran, A. L. and Eubank, T. D., Report 58-3, duPont Co. (1958).
- ⁷⁷ Riley, M. W., *Materials in Design Eng.* **46**, 90 (1957).
- ⁷⁸ Data of Marine Magnesium Div. Merck & Co.
- ⁷⁹ Griffin, W. R., *Rubber World* **136**, 687 (1957).
- ⁸⁰ Griffin, W. R., WADC Tech. Rept. 59-42 (1959).
- ⁸¹ Smith, J. F., *Rubber World* **142**, 102 (1960).
- ⁸² Amith, J. F., *Rubber World* **140**, 263 (1959).
- ⁸³ Gallagher, G. A., Eubank, T. D. and Moran A. L., *Rubber World* **142**, 827 (1960).
- ⁸⁴ Bolstad, A. N., Lo, E. S., and Benning, C. J., M. W. Kellogg Final Rept. to QMC under Contract DA-19-129-QM-1580 (1956).
- ⁸⁵ Abere, J. F., Paper presented at Conf. on Elastomer for Air Weapons (1957).
- ⁸⁶ Simons, J. H., "Fluorine Chemistry", Vol. L, 414, Academic Press (1950).
- ⁸⁷ Borders, A. M., WADC Tech. Rept. 52-197 (1952).
- ⁸⁸ Hamlin, H. C., WADC Rept. 55-381 (1955).
- ⁸⁹ Testroet, R., Rock Island Arsenal Lab. Rept. 59-851 (1950).
- ⁹⁰ Wilson, Angus, Elms, Br. Rept. #6, QMR&E Command (1956).
- ⁹¹ Schweiker, G. C. and Robitschek, P., *J. Polymer Sci.*, **24**, 33 (1957).
- ⁹² Schweiker, G. C., White, R. R. and Deleo, R. N., WADC Tech. Rept. 55-221 (1955).
- ⁹³ Postelnek, W., *Rubber World* **136**, 543 (1957).
- ⁹⁴ Wilson, Angus, Elms, Br. Rept. #13, QMR&E Command (1957).
- ⁹⁵ Dumas, J. B., *Compt. rend.*, **10**, 149 (1840).
- ⁹⁶ Rochow, E. G., "Chemistry of Silicones", 2nd Edit. Wiley & Sons (1951).
- ⁹⁷ Post, H. W., "Silicones & other Organic Silicene Compounds", Reinhold Pub. Corp. (1949).
- ⁹⁸ Fettes, E. M. and others, Thiokol Chem. Corp. Report to QMC under Contract No. DA19-129-QM-1431 (1956).
- ⁹⁹ Pierce, O. R., and McBee, E. T., WADC Tech. Rept. 52-191 Part I and II (1952) and (1953).
- ¹⁰⁰ McBee, E. T. and Pierce, O. R., WADC Tech. Rept. 52-191 Part III (1954).

- ¹⁰⁶ Tarrant, P., Dyckes, G. W., and Wise, D. H., WADC Tech. Rept. 55-220 (1955-58).
¹⁰⁶ Polmanteer, K. E. and Hunter, M., *J. Appl. Polymer Sci.* 1, 3 (1959).
¹⁰⁷ Hasseldine, R. N., Newlands, M. J., and Plumb, J. B., Paper presented at Conf. on Macromolecules, London, England (1961).
¹⁰⁸ Wilson, Angus, *Elas. Br. Report #8, QMR&E Command* (1957).
¹⁰⁹ Dellaria, J. F., Paper presented at Conf. on Elastomers for Air Weapons (1959).
¹¹⁰ Talcott, T. D., Brown, E. D., and Holbrook, G. W., Paper presented at Div. of Rubber Chemistry, ACS (1957).
¹¹¹ Servais, P. C. and Polmanteer, K. E., Paper presented at Div. of Rubber Chemistry, ACS (1959).
¹¹² Brown, H. C. and others, WADC Tech. Rept. 56-234 (1956).
¹¹³ Postelnek, W., *Ind. Eng. Chem.* 50, 1602 (1958).
¹¹⁴ Gibbs, W. E., Paper presented at JANA Conf. on Elastomer R&D (1960).
¹¹⁵ Seaton, J. A., WADC Tech. Rept. 59-427 (1959).
¹¹⁶ Brown, H. C., Paper presented at JANA Conf. on Elastomer R&D (1958).
¹¹⁷ Brown, H. C., WADC Tech. Rept. 59-272, Part II (1960).
¹¹⁸ Tatlow, J. C., *Rubber and Plastics Age*, 39, 33 (1958).
¹¹⁹ Ruff, O., and Giese, Ber. 1936, 69, 598, 684.
¹²⁰ Barr, D. A., and Hasseldine, R. N., *J. Chem. Soc.* 1881 (1955).
¹²¹ Tarrant, P., and others, U. Fla. Rept. to QMC under Cont. DA19-129-QM-500 (1959).
¹²² Crawford, G. H., Rice, D. E. and Montermoso, J. C., Paper presented at 137th ACS Meeting (1960).
¹²³ Crawford, G. H., Rice, D. E. and Montermoso, J. C., Paper presented at JANA Conf. on Elastomer R&D (1960).
¹²⁴ Chabrie, C., *Compt. rend.* 110, 279 (1890).
¹²⁵ Moissan, H., *Compt. rend.* 110, 276, 951 (1890).
¹²⁶ Villard, *Compt. rend.* 111, 302 (1890).
¹²⁷ Barr, D. A. and Hasseldine, R. N., *J. Chem. Soc.* 3424 (1956).
¹²⁸ Crawford, G. H., Rice, D. A. and Landrum, B. F., Paper presented at Gordon Research Conf. on Polymers (1961).
¹²⁹ Crawford, G. H. and Montermoso, J. C., Paper presented at the JANA Conf. on Elastomer R&D (1958).
¹³⁰ Montermoso, J. C., Griffin, C. B. and Wilson, A., Paper presented at JANA Conf. on Elastomers (1960).
¹³¹ Montermoso, J. C. and others, *Rubber and Plastics Age*, 42, 514 (1961).
¹³² Montermoso, J. C., *Chem. Eng. Progress* 57, 98 (1961).
¹³³ Crawford, G. H., *J. Polymer Sci.* 45, 259 (1960).
¹³⁴ Park, J. D., Lacher, J. R. and Stefani, A. P., Paper presented at 140th ACS Meeting (1961).
¹³⁵ Tarrant, P., O'Connor, D. E. and Pisacane, F., Paper presented at 140th ACS Meeting (1961).
¹³⁶ Stefani, A. P., Lacher, J. R. and Park, J. D., Paper presented at JANA Conf. on Elastomers (1960).
¹³⁷ Bergstrom, E. W., Rock Island Arsenal Lab. Rept. 60-188 (1960).

INSTRUMENTAL METHODS FOR THE ANALYSIS OF POLYMERIC MATERIALS

J. MITCHELL, JR. AND S. S. LORD, JR.

E. I. DU PONT DE NEMOURS & CO., EXPERIMENTAL STATION, WILMINGTON, DELAWARE

CONTENTS

	PAGE
I. Introduction.....	1553
II. Infrared spectroscopy.....	1554
A. Polymer identification.....	1554
B. Polymer structure.....	1556
1. Polyethylene.....	1556
2. Polypropylene.....	1558
3. Hydrocarbon elastomers.....	1559
4. Other polymers.....	1559
C. New methods and techniques.....	1560
III. Ultraviolet spectrophotometry.....	1562
IV. Nuclear magnetic resonance spectroscopy.....	1563
A. Wide line studies.....	1563
B. High resolution studies.....	1564
V. Thermal techniques.....	1565
A. Pyrolysis.....	1565
B. Thermogravimetry.....	1567
C. Differential thermal analysis (DTA).....	1568
VI. Miscellaneous techniques.....	1570
VII. References.....	1572

I. INTRODUCTION

Advances in our knowledge of the chemical and physical structure of polymeric substances have been due in large measure to new and improved instrumental methods of analysis. From the standpoint of chemical structure all polymers have at least one functional group, often in low concentration, e.g., an end group. Principal progress has been made, first, in identification of these groups, and, more recently, in their quantitative determination and location within the molecule. In some cases conventional chemical methods have been greatly improved to provide the high sensitivity required for these analyses, particularly for groups such as acid, amine, ester and carbonyl. However, most chemical methods depend on reaction in solution. Often the choice of solvent is limiting, since it must be inert toward both the sample and the reagents as well as be capable of dissolving a significant amount of the material to be analyzed. In many cases a suitable solvent is not available.

Many of these restrictions do not apply to instrumental techniques. Infrared spectrophotometric methods, for example, may be (a) nondestructive and the sample can be recovered for other studies, (b) rapid, often being completed

within several minutes, (c) direct in which films or dispersions can be handled and, therefore, limited solubility is not a problem, (d) capable of providing information on physical as well as chemical structure, and (e) capable of supplying other useful information during the course of an analysis. Examples of techniques used in analyses for chemical and physical structure are:

Chemical Structure	Physical Structure
Chemical Electrochemical	X-Ray Diffraction Electron Diffraction
← Infrared →	
Raman	Internal Friction
Ultraviolet-Visible	Electron Microscopy
Fluorescence, Phosphorescence	Optical Microscopy
← Nuclear Magnetic Resonance →	
Electron Paramagnetic Resonance	Differential Thermal Analysis
Pyrolysis	Rheology
Infrared	Cryoscopy
Mass Spectrometry	Ebulliometry
Gas Chromatography	Osmometry
Thermogravimetry	Light Scattering
Emission Spectroscopy	Ultracentrifugation
X-Ray Spectroscopy	Fractionation
Radiochemical	Miscellaneous Physical Tests

This paper reviews primarily recent advances in instrumental techniques which have been shown to be capable of quantitative analysis for chemical structure. Also, reference is made to the use of infrared spectroscopy, nuclear magnetic resonance spectroscopy, and differential thermal analysis in studies of physical structure. Applications to characterizations of elastomers are emphasized, although for illustrative purposes investigations of other polymers often are discussed.

II. INFRARED SPECTROSCOPY

Infrared spectroscopy has continued to be one of the most useful instrumental techniques for characterizing and analyzing polymers. Several texts and reviews have appeared in recent years which cover applications to elastomers and other polymers as well as infrared analysis in general. The two-volume work by Hummel⁴³, for example, can be of material assistance to one engaged in elastomer identification work. The first volume discusses both chemical and spectroscopic methods of polymer analysis with particular emphasis on infrared, and the second volume is an extensive collection of reference spectra of polymers and additives. For one who is faced with the problem of empirical band identification and assignments, Bellamy's text⁴ is invaluable. Recent reviews which should be of particular interest have included those of Blokh⁶, Potts⁴⁹, Krimm⁵³, and Linnig and coworkers⁴⁸.

A. POLYMER IDENTIFICATION

Most of the recent publications dealing with polymer identification by means of infrared have dealt with techniques for obtaining a tractable sample, improved spectra, or more rapid results. Spectra of commercial polymers and their salient features are readily available from published sources^{40, 43, 56}.

Corish pointed out in some detail the spectral features which enable one to analyze rapidly many different polymers, copolymers, and mixtures of poly-

mers¹⁹ as well as fillers²⁰ by using ultrathin (ca. 2 μ thick) microtomed sections. This technique had the advantage of being more rapid than the destructive methods, and has been used for identifying many different polymers, copolymers, and mixtures of polymers loaded with up to 60 parts phr of carbon black. The technique could be used to identify fillers as well as the base elastomer. The microtoming approach also was used for identifying and analyzing polyurethan rubbers¹⁷. In polyester-based urethans the acid portion of the polyester was identified by crystallinity bands in the spectra of stretched microtomed sections, whereas polyether urethans could be characterized by direct examination of the sections. In either type, the diisocyanate portion could be identified by the skeletal absorptions in the 700–900 cm^{-1} (11–15 μ) region.

Hummel¹⁴ used infrared for the identification of raw rubber, and hard and soft rubber vulcanizates following thermal or solvent degradation of the sample. Using the latter procedure, the sample was extracted for 30 minutes by butanone, followed by 30 minutes milling at high temperature and high friction ratio. Final solution was effected by boiling with *o*-dichlorobenzene to give a syrupy solution which could be coated on a salt plate. Although this method gave excellent results, it proved time-consuming. For example, natural rubber dissolved completely in boiling *o*-dichlorobenzene in 2.5 hours, while neoprene was only 14 per cent dissolved after 26 hours. The pyrolysis technique has been recommended as being more rapid as well as more generally applicable (see p. 1565). The interference of sulfur compounds in hard rubber pyrolyzates was minimized by mixing the sample with an excess of zinc dust or finely powdered calcium prior to pyrolysis (see also p. 1570). Spectra obtained by both techniques, as well as their interpretation, were shown for natural rubber, butyl rubber-butyl blends, Buna-S (SBR), Perbunan (NBR), neoprene, silicone, and Vulkollan.

Smith and McHard¹⁰² summarized the characteristic absorption frequencies of various substituted silicones and showed representative spectra of alkyl and aryl halogenated silicones and polysiloxanes.

Direct infrared analysis of commercial resins often is impractical because of the complex spectra of overlapping bands from plasticizers, stabilizers and fillers as well as the base resin. (An interesting discussion of spectral anomalies resulting from overlapping bands was given by Vandenbelt and Henrich¹⁰³.) Burley and Bennett¹² applied a preliminary extraction-separation scheme for polyvinyl chloride compositions: (a) extracting the plasticizer with ethyl ether, (b) dissolving the resin in tetrachloroethane, and (c) centrifuging to separate filler and stabilizer.

After extraction of the plasticizer, the ether was evaporated and weight of residue determined. Identification was made from the infrared spectrum, either directly or in carbon disulfide solution, by reference to standard spectra^{12, 35, 52, 88}. Some polymeric plasticizers were not extracted completely with ether. Haslam and Squirrell³⁶ used hot methanol following ether extraction for completely removing polypropylene adipate from P.V.C. compositions. Many resins have contained mixtures of plasticizers which could not be analyzed directly from the ether extracts. For such cases Cachia and coworkers¹³ separated the components in the ether extract by liquid-liquid chromatography through a 30 $\text{cm} \times 1$ cm column packed with equal weights of silica gel and Celite. One of three systems was used depending on the nature of the mixture: (a) separation by plasticizer types usually was made by elution with carbon tetrachloride and isopropyl ether, (b) separation of aromatic phosphates from

TABLE I
ANALYTICAL DATA FOR POLYVINYL CHLORIDE RESIN COMPOSITION¹²

Component	Weight per cent			
	Known	Infrared	Emission spect.	Gravimetric
Diethyl phthalate	29.4	30.2 ± 0.2		29.4 ± 0.3
Basic lead carbonate	5.9	6.1	6.7	
Clay	5.9	6.3	6.3	12.55 ± 0.01 ^a
P. V. C. resin	58.8	57.4		58.0 ± 0.3 ^b

^a Total of lead carbonate plus clay.

^b By difference.

aliphatic phosphates was accomplished with benzene and isopropyl ether, and (c) complete separation of phthalates and phosphates, sometimes poorly resolved by method (a), was made with a mixture of carbon tetrachloride, benzene and isopropyl ether.

The resin in the residue from the ether extraction was dissolved in tetrachloroethane¹². Then tetrahydrofuran was added to dilute the viscous resin solution and the resulting mixture was centrifuged to separate filler and stabilizer. The infrared spectrum of the resin was obtained on a film cast from solution while the isolated solids were examined by infrared and emission spectrographic procedures. Spectra were given of several lead containing stabilizers in potassium bromide pellets¹². Spectra of common fillers, such as calcium carbonate, clay and antimony oxide, have been published^{45, 73}. Small amounts of carbon black and inorganic pigments were removed, when necessary, by filtering the resin solution with Celite Filter Aid in a manner similar to that of Dinsmore and Smith for removing carbon black from rubber solutions²².

An indication of precision and accuracy of the method is shown in Table I. This scheme illustrates the general technique for analysis of mixed compositions applicable to a wide variety of materials.

An interesting discussion of the use of infrared spectrophotometry in qualitative and quantitative analyses of coating materials was presented by Fraser, Peacock and Pross²⁸.

B. POLYMER STRUCTURE

Infrared has continued to find a major application in the determination of such polymer structural features as crystallinity, unsaturation, and side-chain characterization.

1. *Polyethylene*.—New methods were developed for determining branching in the polymer chain. Willbourn¹¹² proposed a method for measuring methyl and butyl branches in polyethylene which he developed from studies of hydrocarbon polymers of controlled branching synthesized from diazomethane and its alkyl substituted derivatives. With a double-beam spectrophotometer the methylene absorption at 1365 and 1350 cm⁻¹ (7.33, 7.41 μ) was compensated using in the reference beam a wedge-shaped sample of a very high molecular weight polymethylene assumed to be linear. (Studies by Boyd and Bryant using water vapor as reference⁶⁶ and by Nielsen and Holland⁸³ placed these bands at 1368 and 1352 cm⁻¹, respectively.) The 1378 cm⁻¹ (7.25 μ) — CH₃ band then could be recorded essentially free from interference (Figure 1). The method was used to detect as little as one —CH₃ group per 2000 carbon chain atoms. By extending this technique to butyl and ethyl branches, Willbourn

concluded that low density polyethylene contained primarily ethyl and butyl branches in a 2:1 ratio, and that some high density polyethylenes contained a few branches which appeared to be ethyl groups. A simple method for preparing the wedge-shaped reference sample of polymethylene was described by Harvey and Peters³⁴.

Both the 1368 cm^{-1} ($7.31\text{ }\mu$) and the 1304 cm^{-1} ($7.67\text{ }\mu$) band were associated with the same configuration in the polymer chain³⁵. Experimental observations demonstrated that the intensities of these two bands were strictly proportional to each other³⁶. Boyd and Bryant developed a "self compensation" method for accurately measuring the absorption at 1378 cm^{-1} ($7.25\text{ }\mu$) by total compensation of the 1368 cm^{-1} band as indicated by complete removal of the clearly separated 1304 cm^{-1} band^{46, 56}. This technique was based on the fact that the 1378 cm^{-1} band was unaffected by the crystallinity of the resin while the inter-

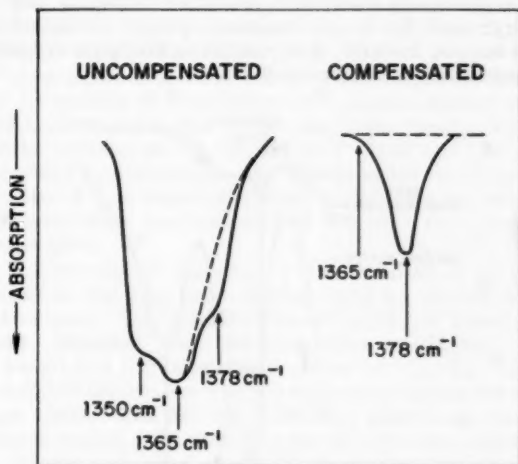


FIG. 1.—Resolution of the 1378 cm^{-1} methyl band: compensation for $1365/1350\text{ cm}^{-1}$ methylene doublet³¹.

fering methylene band decreased in intensity with increasing crystallinity. Self compensation was achieved by placing a carefully annealed film in the sample beam and sufficient shock-cooled film (high amorphous content) in the reference beam of the spectrophotometer to just remove the absorption at 1304 cm^{-1} . Figure 2 compares the scan of the uncompensated sample with that of the self-compensated. Actually perfect compensation was unnecessary, since a simple means was available to correct for incomplete compensation. This was accomplished by pressing one film which was annealed and carefully compensating with shock-cooled films of several thicknesses. A plot was made of apparent absorbance per unit thickness of the 1304 cm^{-1} band against the absorbance per unit thickness at 1378 cm^{-1} . A linear relation with constant slope was obtained which was interpolated (or extrapolated) to the intercept on the ordinate, giving the true absorbance of the methyl band free from interference.

Absorption bands in polyethylene at 895 cm^{-1} (11.18μ) and 888 cm^{-1} (11.25μ) are associated with four-carbon and longer than four carbon alkyl groups, respectively. However, direct measurements were difficult because of interfering absorption by vinyl and vinylidene groups. Vapor phase bromination of the double bonds in the solid sample effectively eliminated this interference⁴⁶, permitting reliable determination of these alkyl groups with the aid of the scale expansion technique¹¹¹.

Krimm⁸⁸ reviewed in detail assignments in the vibrational spectrum of polyethylene.

2. *Polypropylene*.—Several studies have been made of polypropylene resulting in more detailed band assignments as well as proposals for suitable analytical bands for the measurement of isotacticity and crystallinity. Unfortunately, a certain amount of confusion has existed in differentiating between crystallinity and isotacticity. Although the isotactic phase is principally crystalline and the atactic phase is principally amorphous, the terms "isotactic" and "crystalline" are not synonymous^{74, 81}. If one maintains proper control of the thermal history of the sample, however, it is possible to eliminate crystallization rate effects from isotacticity measurements^{10, 69}.

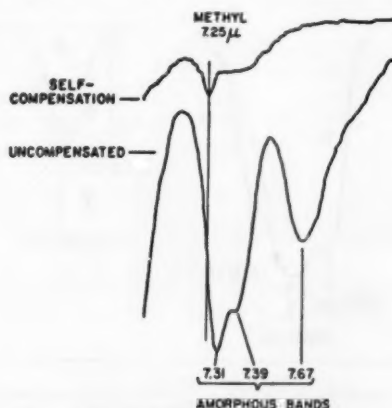


Fig. 2.—Alkyl group determination by self-compensation⁴⁴.

Several workers proposed methods for determining isotacticity based on an absorbance ratio of the $995\text{ cm}^{-1}/974\text{ cm}^{-1}$ ($10.06/10.27\mu$) bands^{1, 69, 92}. In 100 per cent isotactic material, both bands were observed to have the same intensity; in 100 per cent atactic material, the 995 cm^{-1} band appeared only as a weak shoulder and the 974 cm^{-1} band was of the same intensity as the isotactic polymer. The method was claimed to be independent of molecular weight distribution, the physical nature of the sample, and minor amounts of stabilizers⁶⁹.

The use of the $1171\text{ cm}^{-1}/846\text{ cm}^{-1}$ ($8.54/11.82\mu$) band ratio for measuring crystallinity also was suggested⁶⁹ wherein the 1171 cm^{-1} band served as an internal standard. However, it was pointed out that this is not too suitable a reference band since it is actually a doublet with one component originating from the isotactic material and the other from atactic material^{10, 69}. A detailed

interpretation of the spectrum of isotactic polypropylene was made by Liang and Pearson⁶⁷.

Other analytical/reference band pairs that have been suggested include $1167\text{ cm}^{-1}/1153\text{ cm}^{-1}$ ($8.57/8.67\text{ }\mu$)¹, $1167\text{ cm}^{-1}/974\text{ cm}^{-1}$ ($8.57/10.26\text{ }\mu$)¹⁰, $808\text{ cm}^{-1}/974\text{ cm}^{-1}$ ($12.38/10.26\text{ }\mu$)⁹².

Detailed band assignments and classification as amorphous, crystalline and crystallinity-independent were reported by Abe and Yanagisawa¹ and reviewed by Krimm⁶⁸. Liang and others⁶⁶ observed and interpreted polarized infrared spectra of various deuterated polypropylenes in the C—H and C—D regions.

3. *Hydrocarbon Elastomers*.—Several quantitative methods have been proposed for determining unsaturation in polyisoprene. Corish¹⁸ suggested a near infrared method for determining *cis* and *trans*-1,4 repeat units in synthetic polyisoprenes and gutta-rubber mixtures which was claimed to be more accurate than that using the normal infrared region. The method employed the sharp combination band at 4065 cm^{-1} ($2.46\text{ }\mu$) to measure the *cis*-1,4 structure. The absorbance at 4320 cm^{-1} ($2.315\text{ }\mu$) was used as a thickness standard, since it did not vary appreciably with *cis-trans* ratio.

Nel'son³² used bands in the 840 cm^{-1} ($11.9\text{ }\mu$) region for determining the *cis* and *trans* 1,4 content of polyisoprene in a manner similar to that recommended by Richardson and Sacher⁹⁴. The absorption spectra of natural rubber and gutta percha intersect at 857 and 815 cm^{-1} (11.67 and $12.2\text{ }\mu$) permitting calculation of total 1,4-unsaturation. By measuring the absorbance at 843 cm^{-1} ($11.87\text{ }\mu$) the *cis*-1,4 and *trans*-1,4 content could then be calculated. The 1,2- and 3,4-unsaturation was measured at 909 cm^{-1} ($11.0\text{ }\mu$) and 887 cm^{-1} ($11.27\text{ }\mu$), respectively.

Cunneen and coworkers²¹ described a determination of *cis* and *trans* 1,4 structures based on the 1125 cm^{-1} ($8.89\text{ }\mu$) band for *cis* and the 1145 cm^{-1} ($8.73\text{ }\mu$) band for *trans*. The band at 1090 cm^{-1} ($9.18\text{ }\mu$) was used as an internal reference band. Klauzen⁵⁵ used the absorbance at 970 cm^{-1} ($10.31\text{ }\mu$) for determining *trans*-1,4 and the absorbance at 910 cm^{-1} ($11.0\text{ }\mu$) for determining 1,2- in order to follow the reaction of sulfur with rubber during the curing process (see also page 1562). The 935 cm^{-1} ($10.70\text{ }\mu$) absorbance was used as an internal thickness control. By preparing the film on a salt plate and following the spectral changes with time at 143°C , he showed that the sulfur reacts mainly with the 1,4-unsaturation sites.

A quantitative method for determining the unsaturation distribution in polybutadienes was described by Silas and coworkers¹⁰⁰. The *trans*-1,4 and 1,2 (vinyl) unsaturations were measured at 970 cm^{-1} ($10.31\text{ }\mu$) and 710 cm^{-1} ($14.09\text{ }\mu$), respectively. It was found that both the shape and position of the *cis*-1,4 band at 740 cm^{-1} ($13.52\text{ }\mu$) varied with the amount present in the sample. It was measured, therefore, by using an empirical function of the band area.

4. *Other Polymers*.—The molecular structure and infrared band assignments were made for polyvinyl chloride^{68, 80}, polyvinylidene chloride^{68, 79}, and chlorinated polyethylene⁷⁸. Nambu⁷⁸ observed that the direct chlorination of a carbon tetrachloride solution of polyethylene at 70°C resulted in the formation of $-\text{CH}_2-\text{CHCl}-$ and $\text{CHCl}-\text{CHCl}-$ units in the main carbon chain. No $-\text{CCl}_2-$ units were detected.

Quantitative methods were proposed for determining the methyl to phenyl group ratio in silicone polymers^{29, 80, 99} and estimating the hydroxyl groups in dimethyldiphenylsilicone resins⁹⁹. The methyl to phenyl ratio was measured using either the $2940/3000\text{ cm}^{-1}$ ($3.40/3.33\text{ }\mu$) band ratios^{29, 99} or the $1260/1440$

cm^{-1} (7.94/6.94 μ) band ratio⁶⁰. The hydroxyl group was determined as the sum of free and bonded hydroxyl measured at 3600 cm^{-1} (2.78 μ) and 3450 cm^{-1} (2.90 μ), respectively⁹⁹. General reviews of infrared methods for analyzing silicone polymers have been published^{102, 103}, which include summaries of the characteristic frequencies of substituted silicones, as well as representative spectra of alkyl and aryl halogenated silicones and polysiloxanes.

Structural features of polyaldehydes were deduced by Novak and Whalley^{84, 85} from infrared studies. Spectra and band assignments were presented for low-temperature polyformaldehyde, polyformaldehyde- d_2 ⁸⁴ and polychloral⁸⁵ in the $4000\text{--}300 \text{ cm}^{-1}$ (2.5–33 μ) region. In addition, polarized spectra of "Delrin" acetal resin⁸⁴ and polychloral⁸⁵ were shown in the $4000\text{--}450 \text{ cm}^{-1}$ (2.5–22 μ) region. These investigators concluded that the spectra of both the polyformaldehyde and polychloral were consistent with a helical configuration. In the case of polychloral, the chemical formula $\text{HO}(\text{CHCCl}_2\cdot\text{O})_n\text{H}$ was proposed.

The structure of several polyethers was investigated by Kawasaki et al.⁴⁹. They suggested that the major difference between amorphous and crystalline polypropylene oxide was due to rotational isomerism, with the *trans* form in the crystalline portion, and both *trans* and *gauche* forms in the amorphous portion. By observing the CH_2 and CH out-of-plane deformation modes of the vinyl group at 926 and 987 cm^{-1} (10.8 and 10.13 μ) and the open chain C—O—C in the $1150\text{--}1100 \text{ cm}^{-1}$ (8.6–9 μ) region, they suggested that polybutadiene monoxide results from opening the epoxy ring. Polarized spectra suggested that the polymer has a compressed *trans* zig-zag configuration. It was concluded that the structure of polystyrene oxide may be helical, since the shape and intensity of some of the bands is similar to crystalline isotactic polystyrene.

A complete assignment of the normal vibrational modes of the polystyrene molecule was made by Liang and Krimm⁶⁶ and Krimm⁶⁸ using the infrared spectrum of polystyrene from 3200 to 70 cm^{-1} (3.1–140 μ) and Raman frequencies from the literature.

C. NEW METHODS AND TECHNIQUES

The work of Fahrenfort²⁶ on the measurement of "Attenuated Total Reflectance" should be of particular use to polymer analysts. This technique has shown two advantages over conventional reflectance measurements: the sample does not have to be prepared as a thin coating on a reflective surface and the sample does not have to be clear. The spectra obtained have been quite similar to transmission spectra, so that standard transmission collections could be used for identification purposes. Furthermore, it appears that the technique is applicable to at least semiquantitative analysis.

The heart of the ATR system is shown in Figure 3. A hemicylinder of high refractive index, IR-transparent material (AgCl , KRS-5 , etc.) is placed in intimate contact with the sample. The optics are arranged so that the incident radiation is focussed outside the hemicylinder to obtain a fairly parallel light beam inside the crystal. After reflection from the crystal-sample interface, the beam is passed into the monochromator. Provision is made to vary the angle of incidence of the beam on the sample from 15° to 85° . Fahrenfort observed that adjusting the angle of the incident radiation from the strongly refracting dielectric on the interface to somewhat larger than the critical angle results in total reflection only if the sample is nonabsorbing. At those wavelengths where the sample absorbs, the reflection is markedly attenuated. A

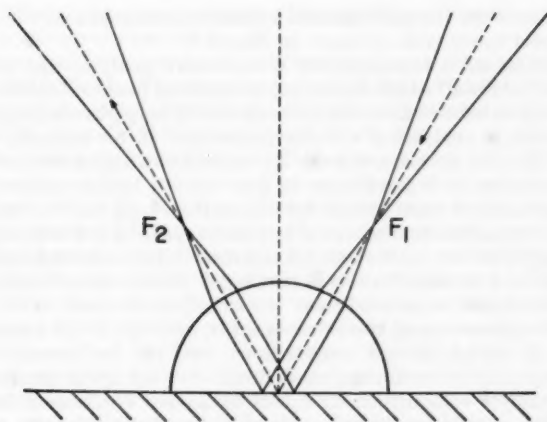


FIG. 3.—The schematic diagram of the ATR reflectance method.

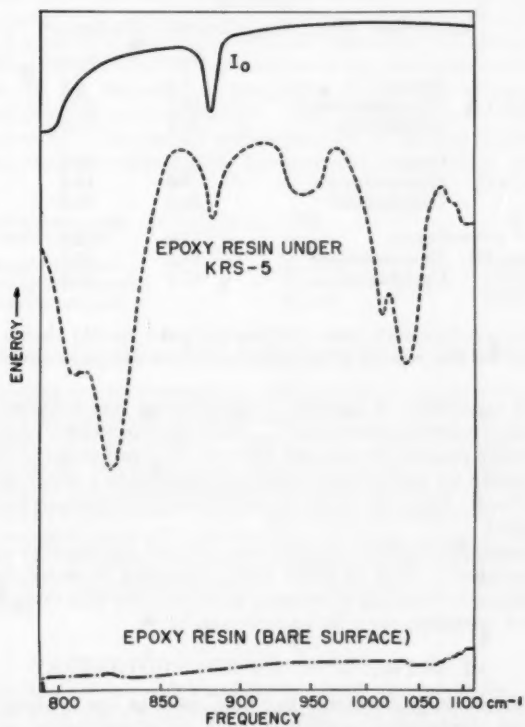


FIG. 4.—Comparison of the ATR reflectance of epoxy resin with the conventional reflectance spectrum.

comparison between the conventional reflection spectrum and the ATR spectrum of a solid epoxy resin is shown in Figure 4.

A new calibration technique for quantitative analysis was proposed by Kimmer and Schmalz⁵⁴ which eliminated the need for pure calibration standards. The authors pointed out that this method should be particularly applicable to isomeric structure analyses of rubbery polymers. If, for example, one desires to measure the 1,2-, *cis*-1,4, and *trans*-1,4 content of a high *trans*-1,4 butadiene-styrene copolymer, it is possible to do this without having pure standards or model compounds of each isomer for calibration. All that is required is to measure the base-line absorbances of a dilution series of the sample solution at the wavelengths where the 1,2-, *cis*-1,4 and *trans*-1,4 structures have absorption bands and to plot the absorbances of each band versus concentration to obtain an "operational extinction coefficient" by extrapolation to $C = 0$. The same procedure is repeated using two other samples, one high in 1,2-content and the other high in *cis*-1,4 (actual compositions need not be known). The nine resulting "operational extinction coefficients" are set up in matrix form and solved for sample composition or actual extinction coefficients for the pure isomers. The application of this method to synthetic mixtures of 1-octene,

TABLE II
ANALYTICAL DATA FOR SYNTHETIC MIXTURES⁵⁴

		Theory	Found	Difference
Mixture I	Octene	5.8	6.1	+0.3
	Dibromobutene	18.1	20.3	+2.2
	Cyclohexene	76.1	74.0	-2.1
Mixture II	Octene	31.2	29.4	-1.8
	Dibromobutene	18.6	13.5	-5.1
	Cyclohexene	50.2	54.2	+4.0
Mixture III	Octene	13.0	12.5	-0.5
	Dibromobutene	54.3	54.8	+0.5
	Cyclohexene	36	37.5	+3.9

trans-1,4-dibromo-2-butene, and cyclohexene gave results shown in Table II. Detailed data on the results of butadiene-styrene analyses have not yet been published.

Improved sensitivity in infrared measurements was achieved by low-cost ordinate scale expansion accessories¹¹¹. With the exception of one potentiometer mechanically coupled to the pen drive of the spectrophotometer, all components including an auxiliary recorder were housed in a separate mobile unit. Expansion of up to fifty-fold in the recorded intensity of absorption bands were readily attained.

An automatic 35 mm slide changer was adapted for use with a double-beam spectrophotometer¹⁴. Two of these units, mounted in series, permitted unattended automatic scanning of as many as 70 polymer film samples, equivalent to 24 hours of operation for a 20-minute scan cycle.

III. ULTRAVIOLET SPECTROPHOTOMETRY

Ultraviolet spectrophotometry has been used in the analysis of polymers principally for determining additives such as antioxidants or accelerators rather than for determining the polymer composition itself. Those polymers

containing UV-absorbing groups may be successfully analyzed, however, if the interfering additives are removed.

Several methods have been proposed recently for analyzing styrene-containing polymers^{25, 41, 42, 107}. The styrene content of methyl methacrylate-styrene copolymers was measured directly at 269 $m\mu$ in chloroform solution¹⁰⁷, since poly(methyl methacrylate) does not absorb above 250 $m\mu$. Residual styrene monomer in polystyrene was determined²⁵ by precipitating the polymer from a chloroform solution with methanol and measuring the absorbance at 245 $m\mu$ of the monomer remaining in solution. Hilton⁴² proposed a method for determining bound styrene in SBR raw polymer, black masterbatches, or cured stocks. The procedure was based on nitrating the polymer with concentrated nitric acid to convert the styrene units to principally *p*-nitrobenzoic acid. The presence of incompletely removed interferences (accelerators, antioxidants, aromatic compounds, and certain heterocyclics) was detected by measuring and calculating the styrene content at three wavelengths (263, 274, and 285 $m\mu$). The accuracy and precision of the method were approximately 1% relative, and it appeared possible to extend the method to styrene-acrylonitrile copolymers, terpolymers, graft polymers, and blends. A shortened procedure was proposed⁴¹ to eliminate lengthy ether extractions from the above method.

Other direct ultraviolet analyses reported recently have included the determination of pyridine in acrylonitrile-methylvinyl pyridine copolymers¹⁰⁴ and the analysis of amino-formaldehyde resins for melamine and thiourea⁷⁶.

A determination of sulfide end groups based on the iodine-sulfide complex absorption at 308 $m\mu$ was used to determine the number average molecular weight of poly(methyl methacrylate)⁹⁶. The following data obtained from samples prepared by a free radical polymerization using each of three different mercaptans as chain transfer agents gave excellent correlation with osmotic data⁹⁸:

Methyl methacrylate model polymers	\bar{M}_n osmotic	\bar{M}_n spectrophotometric
Mercaptoethanol	66,200	70,300
Dodecylmercaptan	71,900	73,250
Benzylmercaptan	65,400	63,900

IV. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY*

Nuclear magnetic or spin resonance (NMR or NSR) has become increasingly important for both physical and chemical structure studies on polymers, primarily associated with proton or F^{19} resonances. Wide line studies have provided information on (a) transitions, (b) crystallinity, (c) rates of crystallization, (d) plasticization and swelling, (e) branching and crosslinking, and (f) bond directions and distances. High resolution investigations, on the other hand, have been used profitably for analyses involving (a) group and molecule identifications, (b) hydrogen bonding, (c) proton exchange reactions, (d) dissociation equilibria of acids and bases, (e) keto-enol tautomerism, and (f) stereoisomerism.

A. WIDE LINE STUDIES

In wide line studies line width and shape usually are measured as functions of temperature. As the temperature is raised, motion within the amorphous

* See also the following article, this issue, by W. P. Slichter.

regions usually increases at a higher rate than in crystalline regions, resulting in distinguishable line narrowing.

Kusumoto, Lawrenson and Gutowsky⁸⁹ obtained line shape and spin relaxation times of some dimethyl silicones over a wide temperature range. Line widths and second moment values for cured Silastic 80, 400 Gum and 200 Fluid were small compared to other elastomers, e.g., line width and second moment for Silastic 80 and natural rubber⁹² at 77° K were 4.5 gauss vs 9.5 and 8.4 gauss² vs 18.5, respectively. These data suggested that considerably more molecular motion, associated with methyl group rotations, occurred in these silicones than in other elastomers. Even though it has a structure similar to that of the dimethyl silicone, polyisobutylene (PIB) exhibited a marked difference in line width at liquid nitrogen temperature, apparently due to extensive interlocking of the methyl groups in PIB which restricted reorientation⁹⁰. However, at temperatures corresponding to the glass transition, the silicones and PIB behaved similarly in that both types showed a considerable increase in motions of chain segments⁸⁹.

Low molecular weight impurities, e.g., water, may seriously affect line widths. The small molecules, being more mobile, will lead to a narrow line superimposed on a broad signal from the solid. Actually, this effect can be used for determining water in solids⁹³. Small amounts of water in nylon caused marked changes in line widths⁹¹. Defects in crystalline regions also may affect molecular motion. Gupta, for example, observed a shift with time in transition temperatures of polyethylene⁹¹.

For further information on wide line studies with particular reference to spin relaxation the reader is referred to the review by Slichter in this volume and to other reviews by Slichter¹⁰¹ and Powles⁹¹. The latter author also discusses high resolution spectra of some polymers.

B. HIGH RESOLUTION STUDIES

Recent investigations of high resolution spectra of polymers in solution promise to supply new details on chemical structure. Bovey, Tiers and Filipovich³, using 40 mc equipment, compared spectra of polystyrene (15 per cent solution in carbon tetrachloride) with cumene. Peaks for the polymer were somewhat broader than those for cumene. However, they were sufficiently narrow to provide pertinent structural information, e.g., the phenyl peak was only 0.005 gauss wide. The aromatic group protons of polystyrene were split into two peaks; the second was apparently due to *o*-protons, based on evidence from studies of chloropolystyrene in which only a single peak was observed. Narrowness of peaks and their constancy with changes in molecular weight indicated that they resulted from segmental motion rather than from motion of the whole polymer molecule. The results indicated motion by segments of about ten monomer units. Similar conclusions were reached by Odajima⁸⁷, who also presented a good theoretical treatment of spin relaxation of protons of PIB in carbon tetrachloride solution.

Bovey and coworkers⁸ studied butadiene-styrene copolymers in carbon tetrachloride solution. Below 88 mole per cent styrene only a single peak was observed for the aromatic group protons. Studies of polymethyl methacrylate^{9, 106} and polymethacrylic anhydride¹⁰⁶ indicated that high resolution spectra permitted discrimination among isotactic, syndiotactic and heterotactic sequences. Figure 5 shows spectra of poly(methyl methacrylate) prepared, re-

spectively, with free radical and anionic initiators⁹. Spectrum *a* showed a single peak for methylene group proton resonance at 8.14 τ , as would be expected for the syndiotactic polymer. Spectrum *b* showed three peaks in the same region, which could be explained by electron-coupled spin-spin splitting. This behavior would be predicted for isotactic polymer in which two protons would be differently shielded. Actually, a four-fold resonance would be expected; in this case the fourth peak probably was located under the α -methyl proton resonance at 8.78 τ . Observation of the methylene group proton resonances gave an absolute, independent confirmation of the structures previously deduced from x-ray fiber diagrams. In addition to supplying information on stereochemical configurations degrees of regularity, block sizes, etc., appear to be determinable⁹.

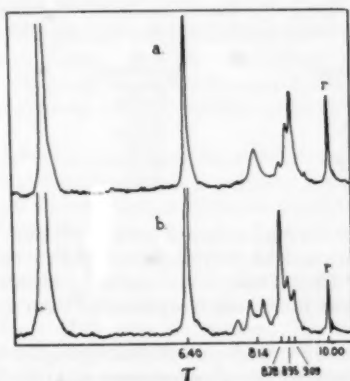


Fig. 5.—NMR spectra of methyl methacrylate polymers prepared with (a) benzoyl peroxide in toluene at 100° and (b) *n*-butyllithium in toluene at -62°. The spectra were obtained on 15% solutions of the polymers in chloroform with 1% tetramethylsilane as reference (*r*)¹.

V. THERMAL TECHNIQUES

A variety of thermal techniques are used for studies of both chemical and physical structure of polymers. Probably the most useful methods are based on pyrolysis, differential thermal analysis and thermogravimetry.

A. PYROLYSIS

Pyrolysis may provide information on (a) kinetics and mechanism of degradation, (b) thermal and oxidative stability, and (c) identity of polymers. To obtain quantitative and reproducible data, conditions must be carefully controlled and the products analyzed rapidly. Hot wire pyrolysis, using only a few milligrams of sample, has been the most convenient and reliable with analyses being made by gas chromatography, mass spectrometry, infrared spectroscopy or thermal conductivity.

Jones and Moyles⁴⁷ cast a thin film of the sample onto a straight wire filament. The unit was designed such that gaseous degradation products were moved by the carrier gas directly onto a gas chromatography column packing. With carrier gas flowing past the sample into the column, the wire filament was

heated quickly to a temperature of about 500° C over a period of two to five seconds. Completeness of degradation was checked by "re-firing" at about 1000° C. "Fingerprint" chromatograms were illustrated for poly(methyl methacrylate), polystyrene and copolymers of methyl methacrylate with styrene and α -methyl styrene, respectively. Degradation products were separated through a column at 80° C containing polyethylene glycol succinate as liquid phase.

Barlow, Lehrle and Robb² used a hot filament connected directly to a gas chromatography column. Auxiliary controls permitted rapid heating for total degradation or stepwise elevation of the temperature. The latter was particularly useful for characterizing homopolymers and copolymers by making use of variations in the temperature dependence of degradation rates. Typical chromatograms were given for a variety of homopolymers, copolymers, and polymer mixtures. The following data illustrate application of this rapid technique to the analysis of vinyl chloride-vinyl acetate copolymers:

By chemical analysis for total Cl (dupl. detns.)	By infrared method ($\pm 1\%$)	By pyrolysis method ($\pm 2\%$)
60.2, 61.4	54.7	55.8
73.8, 74.4	72.3	72.2
77.4, 86.2	84.8	83.9
86.9, 88.9	89.0	87.7

Separations were made through columns packed with dinonyl phthalate (below 100° C), low molecular weight polyethylene (M.P. = 105°, MW = 2500) or silicone oil (100–280° C). These investigators² concluded that the hot wire pyrolysis procedure was more widely applicable than a dielectric breakdown method.

Lehmann and Brauer⁴⁴ used gas chromatography to determine volatile products resulting from pyrolysis of polystyrene and poly(methyl methacrylate) at temperatures from 425 to 1125° C. The pyrolysis chamber was connected directly to a gas chromatography column. From 2- to 3-mg of sample was weighed into a small Vycor boat which was inserted in a platinum wire heating coil. (The pyrolysis chamber was similar to one used previously¹⁰⁶ in which 10- to 15-mg samples of methacrylate copolymers were placed directly on a platinum wire coil.) At 425°, polystyrene degraded almost completely to monomer; at higher temperatures, increasing amounts of ethylbenzene, toluene, benzene, ethylene, and acetylene were formed. From poly(methyl methacrylate) essentially pure monomer was found in volatiles at 425°. At higher temperatures, several other methyl esters were formed together with C₁ and C₂ hydrocarbons and carbon dioxide.

Hot wire pyrolysis with gas chromatographic analysis was used by Guillet and coworkers²⁰ for analyses of methacrylate copolymers. Gas chromatography also was used for separating volatile liquid products from thermal degradation of certain polythiocarbamates²³. In general the products evolved at about 300° C in a nitrogen atmosphere were the thio-analogs of those from corresponding polycarbamates²⁴. Two gas chromatographic columns were employed: (a) a nonpolar liquid phase of silicone 200 oil and (b) a polar phase of Carbowax at 150° C.

Pyrolysis products of acrylate and methacrylate polymers were analyzed by gas chromatography⁹³. Degradation was completed within 30 seconds at 500° C in a helium atmosphere. Separations were made on columns containing.

di-*n*-decyl phthalate, diglycol stearate, or silicone 550 oil. The polymers studied degraded primarily to the monomers, permitting rapid identification and semiquantitative analysis of mixtures.

Infrared analysis of condensable pyrolyzates from a variety of elastomers and other polymers (filled and unfilled) was used successfully by Harms³³. This approach served as a rapid method of identification. (Many filled polymers could not be analyzed directly by conventional infrared transmission procedures.) Included among polymers analyzed were Saran, carbon-filled butyl and Hycar PA rubber, carbon-filled neoprene, and silicones. Cleverly and Hermann¹⁶ used two furnaces set at 200° and 400° C, respectively. About one gram of sample was placed in a tube, which was evacuated to about 0.5 mm Hg. The end containing the sample was placed in the 200° furnace at which temperature most additives were volatilized, condensing along the exposed portion of the tube. The condensate was analyzed by infrared spectrophotometry. Then the process was repeated at 400°; the pyrolyzate usually condensed as a viscous liquid. Spectra were given for pyrolyzates from butadiene-styrene (B-S) copolymers, B-S-natural rubber copolymers, butadiene-acrylonitrile copolymers, natural rubber, polychloroprene, and silicone rubber.

Lady and coworkers^{61, 62} devised a special cell for direct automatic continuous or repetitive infrared scanning while a polymer sample was being heated. In this way the course of degradation or oxidation could be followed by observing changes in the infrared spectrum.

The rapid pyrolysis technique of Rogers and coworkers⁹⁵ was used by Vassallo¹⁰⁹ in rapid, sensitive analyses of organic polymers. Products from hot wire pyrolysis were oxidized to carbon dioxide and water over hot copper oxide. The total CO₂ + H₂O was determined by thermal conductivity. Alternately, CO₂ could be determined separately, after removal of H₂O by silica gel or "Drierite" or the two compounds could be separated by gas chromatography. Pyrolysis products from phenol formaldehyde resin which were synthesized using ¹⁴C-tagged aldehyde were separated by gas chromatography. Carbon dioxide formed by combustion of the fractions was determined by a counting technique⁷⁵.

The composition, within $\pm 2\%$, of ethylene-propylene copolymers and blends was determined by mass spectrometric analyses of their pyrolysis products¹¹. This same technique could be used for other mixtures in which selected mass peaks could be attributed to one of the constituents.

Order of stability of several elastomeric copolymers in both vacuum and oxygen was reported by Wright¹¹² as follows: vinylidene fluoride-hexafluoropropylene > vinylidene fluoride-chlorotrifluoroethylene = perfluoroethylene-1,3-butadiene > hexafluoropentylene adipate-trifluoronitrosomethane.

B. THERMOGRAVIMETRY

Thermogravimetry provides a method for following weight loss as a function of temperature. A comparison of data from pyrolysis studies on poly(methyl methacrylate) by Madorsky⁷⁰ and Vassallo¹⁰⁹ showed that under isothermal conditions decomposition in vacuo and in nitrogen followed nearly the same curve in plots of per cent volatilized vs. temperature. Under programmed temperature (5° C/min) in nitrogen the curve was shifted to 40 to 50° C higher¹⁰⁹.

C. DIFFERENTIAL THERMAL ANALYSIS (DTA)

Recent improvements in instrumentation have made the technique of DTA highly useful for studying phase transitions and chemical reactions involving heat. Discrimination is made readily between exothermic and endothermic activity. An excellent discussion of theory, instrumentation and applications of DTA was given by Ke⁵¹. In practice the temperature difference is plotted between the sample and an inert reference material. Vassallo¹¹⁰ obtained a precision of $\pm 0.3^\circ\text{C}$ over a wide temperature range by using small undiluted samples (as little as 2 mg.) and continuous temperature measurement within the sample. An interesting illustration of the type of information that can be obtained by DTA is shown for tristearin crystallized from the melt (Figure 6)¹¹⁰.

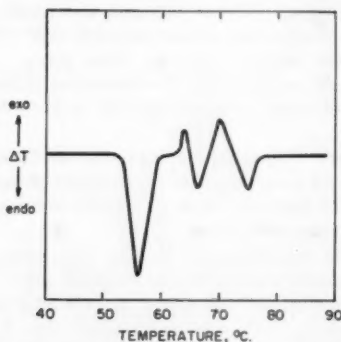


FIG. 6.—DTA scan of tristearin crystallized from the melt¹¹⁰.

On heating, an endotherm at 56°C was observed representing melting of the α -form, followed by recrystallization to the β' -form, melting, conversion to the stable β -form, melting. On cooling, a single exotherm was observed at about 53° , corresponding to the freezing point. When crystallized from solution, tristearin was primarily in the β -form and the thermogram showed a major melting peak at about 75° with evidence for only traces of other polymorphs.

Further illustrations of applications to measurements of melting points, heats and entropies of fusion and crystallinity were described by Ke⁵⁰ for polyolefins. Heats of fusion were calculated for four polyethylenes from areas under the relatively sharp melting peaks, after calibration of the instrument with benzoic acid. Knowing the melting point T_m and heat of fusion ΔH_f , the entropy of fusion was calculated conveniently from the relation,

$$\Delta S_f = \Delta H_f / T_m$$

Data for the polyethylenes studied were⁵⁰:

	M.P., $^\circ\text{C}$	ΔH_f , cal/g	ΔS_f , e.u./g
Marlex 50	135	58.6	0.144
Super Dylan	130	52.2	0.130
Experimental	135	55.7	0.137
DYNH	112	33.6	0.087

Per cent crystallinity (x) was calculated from the equation:

$$x = [(H_a - H_c)/\Delta H_f]100$$

where H_a and H_c were enthalpies of the polymer in the amorphous and crystalline state, respectively, and ΔH_f was the heat of fusion of perfectly crystalline polyethylene. ΔH_f was obtained from the heat of fusion of crystalline *n*-dotriacontane. Degrees of crystallinity obtained by DTA were compared with values reported in the literature⁶⁰:

	% Crystallinity	
	DTA	Literature
Marlex 50	91	93
Super Dylan	81	65-85
Experimental	86	87
DYNH	52	40-60

Mixtures of polyethylene with isotactic polypropylene gave two peaks in the thermogram, the areas of which were proportional to composition⁶⁰. Reproducible shifts in the melting points were observed with change in composition of ethylene-propylene copolymers⁶⁰.

Application to curing was demonstrated for Vibrin 135 resin (mixed polymer of glycol maleate and triallyl cyanurate) synthesized using *tert*-butyl perbenzoate as catalyst⁷⁷. Figure 7 compares thermograms of an uncured sample with samples cured at 80° and at 180° C. Exothermic peaks at about 150° and 180° in samples 1 and 2 appeared due to further polymerization of the polyester. The absence of a peak in this region from sample 3 indicated that this material was completely cured. Peaks at about 320° were thought due to curing of the

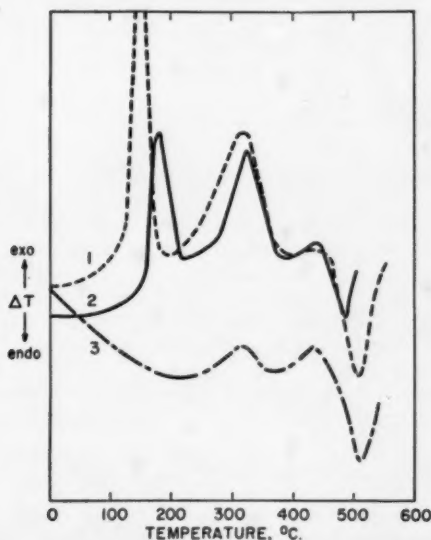


Fig. 7.—Effect of curing in Vibrin 135. (1) uncured sample; (2) sample cured at 80° C for 24 hours; (3) sample cured at 180° C for 24 hours⁷⁴.

triallyl cyanurate fraction of the resin. When benzoyl peroxide was used as catalyst, no exothermic peak was observed in the 150 to 180° region, indicating that essentially complete cure was achieved during polymerization. DTA would appear to be ideal for establishing curing schedules for most polymer systems. This technique should be more specific than most of the empirical methods currently used. Often results by the latter have been affected by impurities or additives, requiring correction when their presence is known or introducing errors when not accounted for. Such problems must be considered even with Chang's method for determining degree of cure of phenolic resin-impregnated materials¹⁵. In this case the cloud point of an acetone extract was determined by titration with distilled water under carefully controlled conditions. The milliliters of water required was equal to an index number indicative of cure.

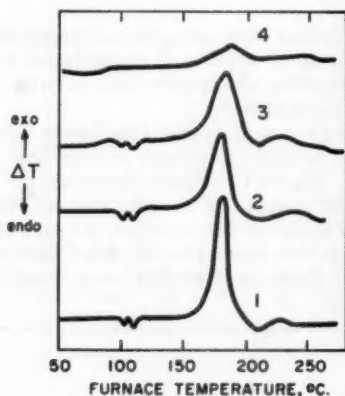


FIG. 8.—Effect of combined sulfur on heat of reaction of 68/32 rubber-sulfur compound: (1) precure: 1 hr at 153° C, (2) precure: 2 hr. at 153° C, (3) precure: 3 hr at 153° C, (4) precure: 4 hr at 153° C⁵.

Figure 8 shows thermograms obtained on a 68:32 rubber-sulfur composition precured for differing times at 153° C⁵. Fully cured ebonite was used as reference material. With increasing precure time, the area under the peak at 185–190° decreased, apparently reflecting an increase in the combination of sulfur with the rubber. The two endothermic changes in the area of 115° were indicated to be due to the enantiomorphous change from α - to β -sulfur and its subsequent melting⁵. Heat of reaction was calculated as 147 cal/g of the mix, after calibration of the instrument from the known heat of dehydration of cupric sulfate pentahydrate⁶.

Further examples of applications of DTA to glass transition measurements and to studies of chemical reactions were reported by Ke⁶¹.

VI. MISCELLANEOUS TECHNIQUES

Subtle changes which occur during the vulcanization of rubber have been indicated by means of fluorescence spectroscopy²⁷. Both the spectral energy distribution and intensity showed a strong dependence on both cure time and temperature. The fluorescence spectra of samples vulcanized at 130°, 145°, 160°, and 175° were obtained, and the intensity of the fluorescence was found to increase with increasing temperature and cure time.

and 151° C for varying lengths of time were excited using 366 m μ radiation from a mercury arc.

Smith and McHard¹⁰² indicated that Raman spectroscopy, although little used in polymer analysis, has several advantages over infrared in the analysis of silicones. It is useful for detecting Si—Br and Si—I stretching vibrations (150–450 cm⁻¹), Si—Si vibrations (weak in the infrared because of symmetry considerations), and double or triple bonds at symmetry centers. Krimm's review on "Infrared Spectra of High Polymers" included information on Raman spectra.⁵⁸

Kratky and Sand⁵⁷ summarized the theory and experimental technique of small angle x-ray scattering for solutions of randomly coiled chain molecules. For crepe natural rubber in hexane solution a persistence length, a , between 5.4 and 6.6 Å was obtained. In diisopropyl ether solution the value was 7.6 Å, consistent with the prediction that the molecule should be more extended in this better solvent. Evidence for aggregate formation was found for crepe and hexane solutions after several weeks' aging at 0° C. NBR in toluene solution gave a persistence value of 9.7 Å.

Zinc oxide in rubber vulcanizates was determined by a rapid, nondestructive x-ray diffraction method⁶⁸. The rate of disappearance of the oxide was independent of the amount and type of filler and degree of crosslinking. Most of the reacted oxide appeared as zinc sulfide.

Alkoxy groups in polymers of acrylates and maleates were determined by the Zeisel method⁷². Alkyl iodides were collected in a cold trap and separated by gas chromatography. Mixtures of methyl, ethyl and butyl iodides were resolved on a 9-ft. \times 0.25 in. stainless steel column at 70° packed with di-2-ethylhexyl sebacate on firebrick. Ethyl acrylate in methyl methacrylate copolymers was determined by gas chromatographic separation of the alkyl iodides⁵⁷.

The oxygen flask combustion method was used in analyses for chlorine in polymers and plasticizers⁵⁸. Oxidation products were absorbed in aqueous caustic containing sodium bisulfite and total chloride determined by potentiometric titration with standardized silver nitrate solution. Results on poly(vinyl chloride) and chlorinated diphenyl compared favorably with those by the lengthy Carius procedure. Oxygen flash combustions of some fluorine-containing polymers were complete in polyethylene bottles employed in place of the usual Pyrex flasks⁴⁸. Fluoride was absorbed in aqueous caustic and determined by the thorium nitrate titration method. Electrical ignition in a closed system was recommended in place of the conventional open flame method for a variety of materials, particularly those which were thermally unstable⁷¹. The oxygen flask technique serves as a rapid decomposition procedure to prepare samples for a variety of elemental analyses.

A sensitive colorimetric test was reported for Co in rubbers, based on intensity of the reddish complex formed on reaction with nitroso-R-salt⁷. No interference was observed from Al, Fe, Mn, Zn, Ca, Mg, Cu, Ni, Pb, or Ti.

A polarographic method was reported for Cu, Mn, and Zn in raw and vulcanized rubbers.³ Spectrographic procedures were described for Mg, Zn, Ca, and Ba in rubber^{58, 97}.

Other information on chemical analyses and physical tests on natural and synthetic rubbers was given in the review by Linnig and coworkers⁶⁸. Recent applications of a variety of techniques to elemental, functional group, and compound analyses were reviewed in the April, 1960 Reviews issue of ANALYTICAL CHEMISTRY.

REFERENCES

- ¹ Abe, K. and Yanagisawa, K., *J. Polymer Sci.* **36**, 536 (1959).
- ² Barlow, A., Lehigh, R. S., and Robb, J. C., *Polymer* **2**, 27 (1961).
- ³ Belitskaya, R. M., *Trudy Nauch.-Issledovatel. Inst. Resin. Prom. Sbornik*, **3**, 123 (1956).
- ⁴ Bellamy, L. J., "The Infrared Spectra of Complex Molecules", John Wiley & Sons, New York, 2nd ed., 1958.
- ⁵ Bhaumik, M. L., Sircar, A. K., and Banerjee, D., *J. Appl. Polymer Sci.* **4**, 366 (1960).
- ⁶ Blokh, G. A. and Mal'nev, A. F., *RUBBER CHEM. & TECHNOL.* **32**, 628 (1959).
- ⁷ Bogina, L. L. and Martuykhina, I. P., *Kauchuk i Rezina* **1959**, (11), 58.
- ⁸ Bovey, F. A., Tiers, G. V. D. and Filipovich, G., *J. Polymer Sci.* **38**, 73 (1959).
- ⁹ Bovey, F. A. and Tiers, G. V. D., *J. Polymer Sci.* **44**, 173 (1960).
- ¹⁰ Brader, J. J., *J. Appl. Polymer Sci.* **3**, 370 (1960).
- ¹¹ Bua, E. and Manaresi, P., *Anal. Chem.* **31**, 2022 (1959).
- ¹² Burley, R. A. and Bennett, W. J., *Appl. Spectroscopy* **14**, 32 (1960).
- ¹³ Cachia, M., Southward, D. W., and Davidson, W. H. T., *J. Appl. Chem.* **8**, 291 (1958).
- ¹⁴ Cassella, J. W., Brame, E. G., and Day, C. E., *Anal. Chem.* **33**, 813 (1961).
- ¹⁵ Chang, J. C. H., *Modern Plastics*, **38**, 117, 120, 190 (1961).
- ¹⁶ Cleverly, B. and Hermann R., *J. Appl. Chem.* **10**, 192 (1960).
- ¹⁷ Corish, P. J., *Anal. Chem.* **31**, 1298 (1959).
- ¹⁸ Corish, P. J., *Spectrochim. Acta* **1959**, 598; *RUBBER CHEM. & TECHNOL.* **33**, 975 (1960).
- ¹⁹ Corish, P. J., *J. Appl. Polymer Sci.* **4**, 86 (1960).
- ²⁰ Corish, P. J., *J. Appl. Polymer Sci.* **5**, 53 (1961).
- ²¹ Cunneen, J. I., Higgins, G. M. C., and Watson, W. F., *J. Polymer Sci.* **40**, 1 (1959).
- ²² Dinsmore, H. L. and Smith, D. C., "The Analysis of Natural and Synthetic Rubber by Infrared Spectroscopy", U. S. Department of Commerce, OTS Publication PB 116704.
- ²³ Dyer, E. and Osborne, D. W., *J. Polymer Sci.* **47**, 349 (1960).
- ²⁴ Dyer, E. and Newborn, G. E., Jr., *J. Am. Chem. Soc.* **80**, 5495 (1958).
- ²⁵ Eisenbrand, J. and Eich, H. W., *Z. anal. Chem.* **175**, 4 (1960).
- ²⁶ Fahrenfort, J., Paper presented at the "European Molecular Spectroscopy Group" congress, Bologna, Sept., 1959; *Spectrochim. Acta* **17**, 698 (1961).
- ²⁷ Faldyash, A. N., Chechik, L. E., and Chugai, A. D., *Kauchuk i Rezina* **17**, No. 8, 28 (1958).
- ²⁸ Fraser, J. G., Peacock, N. M., and Pross, A. W., in C. P. A. Kappelmeier, "Chemical Analysis of Resin-Based Coating Materials", p. 407, Interscience, New York-London, 1959.
- ²⁹ Grant, A. D. and Smith, A. L., *Anal. Chem.* **30**, 1016 (1958).
- ³⁰ Guillet, J. E., Wooten, W. C., and Combs, R. L., *J. Applied Polymer Sci.* **3**, 61 (1960).
- ³¹ Gupta, R. P., *Makromol. Chem.* **42**, 248 (1961).
- ³² Gutowsky, H. S. and Meyer, L. H., *J. Chem. Phys.* **21**, 2122 (1953).
- ³³ Harms, D. I., *Anal. Chem.* **25**, 1140 (1953).
- ³⁴ Harvey, M. C. and Peters, L. L., *Anal. Chem.* **32**, 1725 (1960).
- ³⁵ Haslam, J., Soppett, W. W., and Willis, H. A., *J. Appl. Chem.* **1**, 112 (1951).
- ³⁶ Haslam, J. and Squirrell, D. C. M., *Analyst*, **80**, 871 (1955).
- ³⁷ Haslam, J., Hamilton, J. B., and Jeffs, A. R., *Analyst* **83**, 66 (1958).
- ³⁸ Haslam, J., Hamilton, J. B., and Squirrell, D. C. M., *J. Appl. Chem.* **10**, 97 (1960).
- ³⁹ Heinen, W., *J. Polymer Sci.* **38**, 545 (1959).
- ⁴⁰ Hershenson, H. M., "Infrared Absorption Spectra", Academic Press, New York, 1959.
- ⁴¹ Hilton, C. L., *Rubber Age* **85**, 783 (1959).
- ⁴² Hilton, C. L., Newell, J. E., and Tolmsa, J., *Anal. Chem.* **31**, 915 (1959).
- ⁴³ Hummel, D., "Kunststoff-, Lack- und Gummi-Analyse", Carl Hanser, Verlag, Munich, 1958.
- ⁴⁴ Hummel, D., *Kautschuk u. Gummi* **11**, WT 185, 1958; *RUBBER CHEM. & TECHNOL.* **32**, 854 (1959).
- ⁴⁵ Hunt, J. M., Wisherd, M. P., and Bonham, L. C., *Anal. Chem.* **32**, 1478 (1960).
- ⁴⁶ Johnson, D. R., paper presented at 138th ACS Meeting, New York, Sept. 15, 1960.
- ⁴⁷ Jones, C. E. R. and Moyles, A. F., *Nature* **189**, 222 (1961).
- ⁴⁸ Kanner, H. R. and Carmody, J. N., *J. Appl. Polymer Sci.*, **4**, 248 (1960).
- ⁴⁹ Kawasaki, A., Furukawa, J., Tsuruta, T., Saegusa, T., Kakogawa, and Sakata, R., *Polymer* **1**, 315 (1960).
- ⁵⁰ Ke, B., *J. Polymer Sci.* **42**, 15 (1960).
- ⁵¹ Ke, B., in Mitchell, J., Jr., Kolthoff, I. M., Proskauer, E. S., and Weissberger, A., "Organic Analysis", Vol. IV, p. 361, Interscience, New York-London, 1960.
- ⁵² Kendall, D. N., Hampton, R. R., Hausdorff, H., and Priester, F., *Appl. Spectroscopy* **7**, 179 (1953).
- ⁵³ Khebnikova, L. Ya. and Setkina, O. N., *Sbornik Nauch. Trudov Leningrad Inst. Technol. Mekh i Optiki Mat. Nauk. Khim.*, **1957**, (24), 140.
- ⁵⁴ Kinner, W. and Schmalz, E. O., *Z. anal. Chem.* **170**, 132, (1959); *RUBBER CHEM. & TECHNOL.* **33**, 639 (1960).
- ⁵⁵ Klausen, N. A. and Dogadkin, B. A., *RUBBER CHEM. & TECHNOL.* **33**, 208 (1960); *Fisicheski Sbornik* **1957**, (3), p. 428.
- ⁵⁶ Koenig, J. L., paper presented at ASTM Committee D-20 Meeting, Louisville, Ky., March 8, 1961.
- ⁵⁷ Kratky, O. and Sand, H., *Kolloid Z.* **172**, 18 (1960).
- ⁵⁸ Krimm, S., *Advances in Polymer Sci.*, **2**, 51 (1960).
- ⁵⁹ Kusumoto, H., Lawrenson, I. J., and Gutowsky, H. S., *J. Chem. Phys.* **32**, 724 (1960).
- ⁶⁰ Lady, J. H., Bower, G. M., Adams, R. E., and Byrne, F. P., *Anal. Chem.* **31**, 1100 (1959).
- ⁶¹ Lady, J. H., Adams, R. E., and Kesse, L., *J. Appl. Polymer Sci.* **3**, 65 (1960).
- ⁶² Lady, J. H., Kesse, L., and Adams, R. E., *J. Appl. Polymer Sci.* **3**, 71 (1960).
- ⁶³ Laning, S. H., Wagner, M. P., and Sellers, J. W., *J. Appl. Polymer Sci.* **2**, 225 (1959); *RUBBER CHEM. & TECHNOL.* **33**, 890 (1960).
- ⁶⁴ Lehmann, F. A. and Brauer, G. M., *Anal. Chem.* **33**, 673 (1961).
- ⁶⁵ Liang, C. Y. and Krimm, S., *J. Polymer Sci.* **27**, 241 (1958).
- ⁶⁶ Liang, C. Y., Lytton, M. R., and others, *J. Polymer Sci.* **47**, 139 (1960).
- ⁶⁷ Liang, C. Y. and Pearson, F. G., *J. Molec. Spectroscopy* **5**, 290 (1960).
- ⁶⁸ Linnig, F. J., Tryon, M., and Parks, E. J., *Anal. Chem.* **33**, 127R (1961).
- ⁶⁹ Luongo, J. P., *J. Appl. Polymer Sci.* **3**, 302 (1960).
- ⁷⁰ Madoraky, S. L., *J. Research Natl. Bur. Stds.* **62**, 219 (1959).
- ⁷¹ Martin, A. J. and Deveraux, H., *Anal. Chem.* **31**, 1932 (1959).
- ⁷² Miller, D. L., Samel, E. F., and Cobler, J. G., *Anal. Chem.* **33**, 677 (1961).
- ⁷³ Miller, F. A. and Wilkens, C. H., *Anal. Chem.* **24**, 1253 (1952).
- ⁷⁴ Miller, R. L., *Polymer* **1**, 135 (1960).

- ⁷⁵ Misyev, V. D., Neyman, M. B., and Raspopova, Te. N., *Plasticheskiye massy* 1960, (6), 11; through English abstr. Soviet Bloc and Mainland China Tech. J., Ser. II, No. 2, U. S. Dept. Commerce, p. 31 (March 1961).
- ⁷⁶ Morath, J. C. and Woods, J. T., *Anal. Chem.* 30, 1437 (1958).
- ⁷⁷ Murphy, C. B., Palm, J. A., Doyle, C. D., and Curtiss, E. M., *J. Polymer Sci.* 28, 447, 453 (1958).
- ⁷⁸ Nambu, K., *J. App. Polymer Sci.* 4, 69 (1960).
- ⁷⁹ Narita, S., Ichinohe, S., and Enomoto, S., *J. Polymer Sci.* 37, 251, 263 (1959).
- ⁸⁰ Narita, S., Ichinohe, S., and Enomoto, S., *J. Polymer Sci.* 37, 273, 281 (1959).
- ⁸¹ Natta, G., *Soc. Plastics Eng. J.* 15, 373 (1959).
- ⁸² Nelson, K. V., *Primenenie Metodov Spektroskopii v Prom. Prodoovol'stven. Tovarov i Sel'sk. Khoz., Leningrad. Gosudarst. Univ. im. A. A. Zhdanova, Materialy Soveschaniya, Leningrad 1955*, 67 (Pub. 1957); through *Chem. Abstr.*, 53, 23034 (1959).
- ⁸³ Nielsen, J. R. and Holland, R. F., *J. Molecular Spectroscopy* 4, 488 (1960).
- ⁸⁴ Novak, A. and Whalley, E., *Trans. Faraday Soc.* 55, 1484 (1959).
- ⁸⁵ Novak, A. and Whalley, E., *Trans. Faraday Soc.* 55, 1490 (1959).
- ⁸⁶ Nyquist, R. A., "Infrared Spectra of Plastics and Resins", The Dow Chemical Co., Midland, Mich., 1960.
- ⁸⁷ Odajima, A., *J. Phys. Soc. (Japan)* 14, 777 (1959).
- ⁸⁸ Plasticizers, Commercial Spectra, Sadtler Research Laboratories, Phila., Pa.
- ⁸⁹ Potts, W. J., ASTM, Special Technical Publication No. 247, 225, (1959).
- ⁹⁰ Powles, J. G., *Proc. Phys. Soc. (London)* 69, 281 (1956).
- ⁹¹ Powles, J. G., *Polymer* 1, 219 (1960).
- ⁹² Quynn, R. G., Riley, J. L., Young, D. A., and Noether, H. D., *J. Appl. Polymer Sci.* 2, 166 (1959).
- ⁹³ Radell, E. A. and Strutz, H. C., *Anal. Chem.* 31, 1890 (1959).
- ⁹⁴ Richardson, W. S. and Sacher, A. J., *J. Polymer Sci.* 10, 353 (1953).
- ⁹⁵ Rogers, R. N., Yasuda, S. K., and Zinn, J., *Anal. Chem.* 32, 672 (1960).
- ⁹⁶ Rosenthal, I., Frisone, G. J., and Coberg, J. K., *Anal. Chem.* 32, 1713 (1960).
- ⁹⁷ Setkina, O. N. and Uryan, R. S., *Kauchuk i. Rezina* 18, (3), 10 (1959); *Soviet Rubber Technol.* 3, 10 (1959).
- ⁹⁸ Shaw, T. M., Elaken, R. H., and Kunaman, C. H., *J. Assoc. Official Agr. Chemists* 36, 1070 (1953).
- ⁹⁹ Shull, E. R., *Anal. Chem.* 32, 1627 (1960).
- ¹⁰⁰ Silas, R. S., Yates, J., and Thornton, V., *Anal. Chem.* 31, 529 (1959).
- ¹⁰¹ Slichter, W. P., *Advances in Polymer Sci.* 1, 35 (1958); *Makromol. Chem.*, 34, 67 (1959); *Soc. Plastic Engineers' J.* 15, 303 (1959).
- ¹⁰² Smith, A. L. and McHard, J. A., *Anal. Chem.* 31, 1174 (1959).
- ¹⁰³ Smith, J. C. B., *Analyst*, 85, 465 (1960).
- ¹⁰⁴ Stafford, C., Jr., and Toren, P. E., *Anal. Chem.* 31, 1687 (1959).
- ¹⁰⁵ Strassburger, J., Brauer, G. M., Tryon, M., and Fornati, A. F., *Anal. Chem.* 32, 454 (1960).
- ¹⁰⁶ Tiers, G. V. D. and Bovey, F. A., *J. Polymer Sci.* 44, 479 (1960).
- ¹⁰⁷ Tobolsky, A. V., Eisenberg, A., and O'Driscoll, K. F., *Anal. Chem.* 31, 203 (1959).
- ¹⁰⁸ Vandenberg, J. M. and Heinrich, C., *Appl. Spectroscopy* 7, 171 (1953).
- ¹⁰⁹ Vassalo, D. A., paper presented at 139th. ACS Meeting, St. Louis, March 24, 1961; *Anal. Chem.* 33, 1823 (1961).
- ¹¹⁰ Vassallo, D. A., *Anal. Chem.* 34, 132 (1962).
- ¹¹¹ Westneat, D. F., *Anal. Chem.* 33, 812 (1961).
- ¹¹² Willbourn, A. H., *J. Polymer Sci.* 34, 569 (1959).
- ¹¹³ Wright, W. W., paper presented during Symposium on "High Temperature and Thermal Degradation of Polymers", London, September 21-23, 1960.

NUCLEAR MAGNETIC RESONANCE STUDIES OF ELASTOMERS

W. P. SLICHTER

BELL TELEPHONE LABORATORIES, MURRAY HILL, NEW JERSEY

CONTENTS

	PAGE
I. Introduction	1574
II. General principles	1575
A. The phenomenon of nuclear magnetic resonance	1575
B. Relaxation processes	1577
C. Effects of motion	1580
D. Motion in polymers	1584
E. The measurement of T_1 and T_2	1584
III. Studies of the rigid lattice	1585
A. Early studies	1585
B. Polyisoprenes	1586
C. The second moment of the resonance	1589
IV. Studies of the rubbery state	1593
A. Natural rubber	1593
B. Polyisobutylene	1595
C. Effects of pressure	1596
D. Molecular mobility near the glass temperature	1598
V. References	1600

I. INTRODUCTION

The remarkable property that we associate with rubberlike elasticity, the high degree of elastic deformability, has long been known to arise from molecular motion. In fact, Joule recognized a century ago that the retractive force in stretched rubber stems from thermal motions of molecules rather than from attractive forces between molecules, a conclusion which was all the more remarkable because Joule had no idea of the polymeric nature of rubber. This review tells of the newest technique for studying molecular motion, nuclear magnetic resonance spectroscopy (NMR), and of its application to studies of rubberlike substances.

Appropriately, the most important measurements of rubberlike elasticity have been mechanical—creep, stress relaxation, dynamic response. The viscoelastic properties have been studied theoretically and have been measured profusely. They have told us much about the spectra of relaxation processes, which range over many decades of frequency. However, the mechanical experiments occur at the macroscopic level. Conclusions as to behavior at the molecular level depend upon the soundness of models. Plainly it is also valuable to examine motion directly at the molecular level. There are several techniques that accomplish this end. Infrared spectroscopy and dielectric

relaxation studies are two kinds of measurement that directly indicate the motion of atoms and molecules.

To these techniques is added nuclear magnetic resonance spectroscopy. This method responds to molecular behavior quite differently from other kinds of measurement, and avoids some of the restrictions encountered in these other techniques. For example, the requirement of a permanent electric dipole moment effectively excludes dielectric measurements for the study of *pure* natural rubber and other hydrocarbons, yet motion in such substances is readily seen by NMR. On the other hand, there are distinct limitations to the use of nuclear resonance, as we shall note.

In this paper, we shall review the phenomenon of nuclear magnetic resonance, with emphasis on its use in studies of molecular motion in elastomers. It would be wrong to say that NMR has achieved the importance of the principal physical techniques used to study elastomers. Indeed, the information on elastomers yielded by NMR consists largely of isolated examples. Still, we shall seek to show that the method is powerful and has great potentialities. For a more detailed review of the fundamental physics than is given here, the reader is referred to the excellent paper by Pake¹. A comprehensive survey of NMR studies of polymers is given by Powles².

II. GENERAL PRINCIPLES

A. *The phenomenon of nuclear magnetic resonance.*—The phenomenon depends upon a fundamental property possessed by certain atomic nuclei. In addition to the familiar properties of mass and charge, these nuclei possess angular momentum (spin). This angular momentum is accompanied by a magnetic moment. That is, the nucleus behaves as if it were a little magnet. The property of spin was of course first identified in the electron. The magnetic moment of the electron is the source of the familiar phenomena of paramagnetism and ferromagnetism. The corresponding property in nuclei is 1/2000 as strong, or even less. There are some 130 isotopes, representing more than 80 elements, that exhibit nuclear spin and magnetic moment. From the chemist's viewpoint, the most important of these isotopes is hydrogen. We shall therefore consider only the magnetic resonance of the proton, although the generalities to be given here apply to the other ~ 130 magnetic isotopes as well.

An elemental magnet such as the proton will interact with an applied magnetic field, such as that from a laboratory magnet. It is a fundamental fact that in the presence of an applied magnetic field, the energy of the proton becomes altered, the new values of the energy being explicit quantities above and below the value for the field-free particle. This change in energy depends on the strength of the external field. The difference in energy between the two states, ΔE , is given by

$$\Delta E = 2\mu H_0 \quad (1)$$

where μ is the magnetic moment of the proton and H_0 is the strength of the applied field. Transitions occur between the two states, with the absorption or emission of energy ΔE . In the usual way, this energy may be expressed in terms of a frequency, ν_0 , and the Planck constant, h . Equation (1) then becomes

$$h\nu_0 = 2\mu H_0 \quad (2)$$

This expression links the frequency of the electromagnetic radiation, absorbed or emitted, and the strength of the applied magnetic field. Note that either ν_0 or H_0 can be the independent variable. If we set the field at H_0 , there is just one frequency, ν_0 , at which the proton will absorb or emit electromagnetic energy. On the other hand, if the radiation frequency is set, energy is transferred only when the magnetic field assumes the value H_0 . Because the energy transitions depend in this explicit way on the magnetic field, the effect is termed *magnetic resonance*.

We should comment on the magnitudes involved. Typical laboratory magnets operate in the range of 5000 to 15,000 gauss. If H_0 is 10,000 gauss, for example, the resonant transition given in Equation (2) occurs at a radiation frequency of 42.577 mc/sec in the case of the proton. For other isotopes the resonance occurs at other frequencies. For instance, at this same value of H_0 the resonance of the fluorine nucleus is 40.07 mc/sec, and the resonance of the phosphorus nucleus is 17.24 mc/sec. The three isotopes of hydrogen resonate

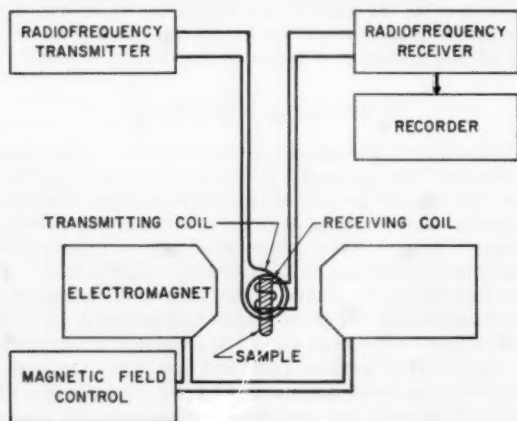


FIG. 1.—Schematic view of nuclear magnetic resonance apparatus.

at different frequencies. Indeed, there are no known isotopes that coincide precisely in resonant frequency for a given value of H_0 .

With typical laboratory magnets, the resonances all occur in the radio-frequency portion of the electromagnetic spectrum. We are dealing with an authentic form of spectroscopy, except that the apparatus consists of radio equipment instead of optical components. We need not discuss the experimental arrangements in any detail. Figure 1 shows schematically the essential features of the apparatus. The sample is placed within a coil of wire which is connected to a radio transmitter and which is situated between the poles of an electromagnet. Although either the radio frequency or the magnetic field strength may be the independent variable, it is usually found convenient to fix the frequency ν_0 and to vary the magnetic field through the resonant value. When the magnetic field is made to pass through the value H_0 , the sample absorbs energy from the transmitter and the nuclei affected pass into a higher energy state. As the excited nuclei return to the ground state the energy is

emitted and picked up by the receiver. This effect is the resonance, and the absorption is commonly called a "line", in analogy to the absorptions in optical spectroscopy.

We should note in passing that the fact of the low frequencies in NMR radiations carries with it a special significance for studies of thermal motions in molecules. That is, the energies involved in these transitions are tiny compared with the energies of molecular motion, at all temperatures except the lowest. Thus, a quantum of energy in NMR is about 10^{-7} as large as a quantum of energy involved in a typical lattice vibration or rotation, seen in the infrared portion of the electromagnetic spectrum. This contrast is important, for it means that when we use NMR measurements to study molecular motion, we can safely presume that the motions are not perturbed.

B. Relaxation processes.—In the absence of an external magnetic field, there is no preference for one or the other of the two states of the proton, for they correspond to the same energy. Application of a magnetic field favors the lower state over the upper state. At equilibrium, the relative populations of the states are described by the Boltzmann relation, which in this case takes the form

$$\frac{N_-}{N_+} = \exp(\Delta E/kT) = \exp(2\mu H_0/kT) \quad (3)$$

where N_+ and N_- are the numbers of protons per unit volume in the upper and lower states, respectively. With ordinary temperatures and field strengths, the exponent $2\mu H_0/kT$ has a magnitude of $\sim 10^{-5}$. The lower state therefore exceeds the upper state in population by only about 10^{-5} per cent. This small margin is important, however, for if the populations were equal there would be no possibility for the net absorption of energy, and the NMR experiment could not take place.

Suppose we have a sample containing protons, in a magnetic field H_0 . Then let the sample be irradiated with a radiofrequency field at the frequency ν_0 . Protons in the lower state will absorb energy, and will consequently transfer to the upper state. Simultaneously, protons in the upper state will emit energy, thereby transferring to the lower state. The rate of absorption of radiation will initially exceed the rate of emission, since at the start there is a small excess of protons in the lower state. However, this excess of population in the lower state will dwindle as the absorption continues. Unless some other process intervenes, the populations of the two states will become equal, with absorption and emission occurring at the same rates, and with no *net* absorption of radiation. The offsetting process is the transfer of energy from the excited nuclei to their surroundings. The term "lattice" is used in the parlance of NMR spectroscopy to identify the assembly of atoms or molecules containing the magnetic nuclei. We take "lattice" to mean not only crystalline arrays, but also other states of matter, such as liquids or solutions. The transfer of energy from the excited nuclei to their surroundings is presumed to occur exponentially in time, i.e., as a first-order rate process, and is described by a characteristic time constant, T_1 , which is called the *spin-lattice relaxation time*. We shall see presently that the relaxation process is related to the motion within the lattice. From the definition, we note that a long T_1 indicates an inefficient exchange of energy from the nuclear spins to the lattice. Depending upon the nature of the sample, values of T_1 fall in a wide range, from milliseconds to the scale of hours.

It is pertinent to note in passing that in terms of Equation (3), the condition of nearly equal populations ($N_+ = N_-$) in the presence of a strong magnetic field corresponds formally to a very high temperature. The temperature here is that of the assembly of nuclear spins, not that of the molecules of which the nuclei are part. It is legitimate to think of a *spin temperature*, as distinguished from a *lattice temperature*, because the interactions between the spins and the lattice are ordinarily small compared with the interactions among the spins themselves or the thermal interactions within the lattice. In terms of the spin temperature, then, the effect of shining resonant energy upon the sample is to heat the assembly of spins. Conversely, the effect of the spin-lattice (T_1) interactions is to cool the nuclear spin system to the temperature of the surrounding lattice. Our earlier conclusion that NMR experiments inflict no perturbation upon the motion of molecules can be stated in the present context by saying that the nuclear spin system has a very small heat capacity.

In addition to the interaction between the nuclei and their environment, there is also an interaction among the nuclei themselves. The effect arises in the following way. Each proton "sees" not only the field of the laboratory magnet, but also the magnetic fields contributed by the magnetic moments of other protons in the neighborhood. These local fields supplement the applied field, positively or negatively. In fact, we may rewrite Equation (2):

$$h\nu_0 = 2\mu(H_0 \pm H_{loc}) \quad (4)$$

The local field, H_{loc} , adds to or subtracts from the laboratory field, depending upon the orientations of the magnetic moments. The local field varies in magnitude as

$$H_{loc} = 3\mu r^{-3}(3\cos^2\theta - 1) \quad (5)$$

where r is the internuclear distance and θ is the angle between the internuclear vector and the direction of the applied field, H_0 .

The local field arising from the magnetic moment of a proton has a strength of about 5 gauss at a distance of 1 Å. By comparison, we have already noted that the field strengths of laboratory magnets are of the order of 10,000 gauss. The local fields therefore may contribute a modest but significant amount to the total field experienced by a given nucleus. In a solid, the interactions between nuclei are numerous and cover a range of values in field strength. Consequently, if we use a single value of radio frequency, we find that resonances occur over a spread of several gauss in the applied magnetic field, corresponding to the range in local field. The resonances are so numerous that they form a continuous distribution, composed of a multiplicity of discrete resonances which are merged into a broad envelope.

Even though such an envelope is generally devoid of features (Figure 2a), it nevertheless is an explicit composite of many resonances and is obtained reproducibly. To characterize the resonance, we commonly resort to some simple figure of merit. The quantity most often used is the *line width*, which may be defined as the span between points of maximum positive and negative slope on the resonance envelope. This is a convenient quantity, because ordinarily the NMR spectrometer is made to yield, for instrumental reasons, not the resonance envelope itself, but rather the *derivative* of the absorption with respect to the magnetic field (Figure 2b). The width of the resonance, as defined above, therefore corresponds to the span between extrema of the derivative curve.

There are other ways of defining the width of the resonance. For example, we could define it as the span of the envelope at a level of intensity corresponding to half of the peak value. Detailed definitions are useful only when the resonance can be described by some convenient analytic function, as for example the function that describes the response of a damped oscillator to sinusoidal excitation, the so-called Lorentzian function. The resonance envelopes found for liquids approximate the Lorentzian function quite well, but those encountered with solids are ordinarily not adequately described by any convenient function. Therefore, we are usually satisfied with the line width defined in the preceding paragraph, since it emerges easily from the experiment as ordinarily performed.

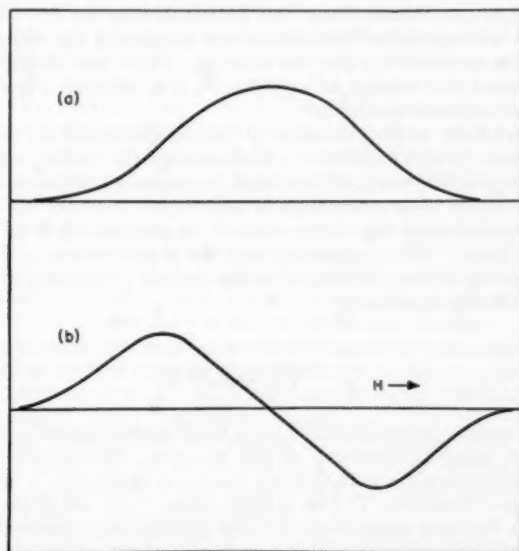


FIG. 2.—(a) The NMR absorption as a function of the applied magnetic field; (b) the derivative of the absorption with respect to the magnetic field.

We have already considered the interactions between the nuclei and the lattice in terms of a relaxation process. We may also look upon the spin-spin interactions, which lead to the line broadening, in terms of a relaxation process. Because of the equivalence between frequency and magnetic field, Equation (2), it is apparent that the line width, δH , can be expressed in terms of a frequency span, $\delta \nu$:

$$\delta \nu = \frac{2\mu \cdot \delta H}{h} \quad (5)$$

Clearly, this quantity represents the spread in the resonant radiofrequency corresponding to the spread in magnetic field arising from the effects of the local fields. Equally well, since frequency has the dimensions of reciprocal

time, we may write the frequency spread in terms of a characteristic time, T_2 :

$$\frac{1}{T_2} = 2\pi \cdot \delta\nu = \frac{4\pi\mu \cdot \delta H}{h} \quad (6)$$

Since the effect producing the spread in the resonant magnetic field and in the resonant frequency arises from interactions between nuclear spins, T_2 is called the *spin-spin relaxation time*.

There is some arbitrariness in T_2 as we have defined it here, for the quantity depends upon our definition of the line width. However, it is entirely satisfactory to consider T_2 somewhat loosely as being inversely proportional to the spread in local fields, H_{loc} , which produce the observed width of the resonance envelope. It is not obvious from this approach why we call T_2 a *relaxation time*. There are equivalent treatments that emphasize the relaxation process inherent in the quantity T_2 (see, for example, Pake¹ and Slichter²). For the purposes at hand, it is enough to regard $1/T_2$ as a measure of the coupling between nuclear magnetic moments.

We return briefly to the discussion of the populations of the states occupied by the protons. It was pointed out, in discussing the Boltzmann distribution given by Equation (3), that the lower state possesses a certain excess in population over the upper state when there is equilibrium between the nuclear spins and the lattice, but that this excess tends to be reduced when the nuclear spin system is irradiated. The surplus population n in the lower state in the presence of a resonance r.f. field H_1 is related to the surplus population at equilibrium, n_0 , by the following expression⁴:

$$\frac{n}{n_0} = \frac{1}{1 + \gamma^2 H_1^2 T_1 T_2} \quad (7)$$

Here γ is the nuclear gyromagnetic ratio, a fundamental quantity that is proportional to the magnetic moment of the nucleus. (Specifically, for protons $\gamma = 4\pi\mu/h$, where again μ is the proton magnetic moment).

We see from Equation (7) that a large value of H_1 will reduce the surplus population in the lower state relative to the population at thermal equilibrium. This situation corresponds to a high spin temperature, as defined by Equation (3). This phenomenon of the disturbance of the surplus spin population is called *saturation*⁴, and the denominator in Equation (7) is called the *saturation factor*. It is seen that susceptibility to saturation depends in part on T_1 and T_2 . Thus, a narrow resonance (large T_2) is relatively more susceptible to saturation than a broad resonance (small T_2), if both have comparable T_1 's.

C. Effects of motion.—The quantities T_1 and T_2 are indeed fundamental to the behavior of the nuclear resonance. As we shall now see, these parameters depend greatly on the kind and extent of molecular motion, but differ in how they depend on the motion.

We consider first the line-broadening interactions which are characterized by T_2 . We have seen that these effects have their source in the local fields created at one nucleus owing to the proximity of other magnetic nuclei. The effect of molecular motion upon these interactions will be considered in purely descriptive terms. Visualize an observer who travels on a proton that moves slowly through the lattice. He will then see all the deviations that occur in the magnetic field, stemming from the positive and negative contributions that the

other protons impose upon the applied field. However, if the observer moves through the lattice more rapidly, these positive and negative fluctuations will seem to compensate one another. When the observer moves through the lattice rapidly enough, these fluctuations will appear to vanish. Thus, the motion will tend to obliterate the influences that lead to line broadening, and the resonance envelope will therefore become progressively narrower as the motion becomes more rapid and extensive. It may be shown¹ that the resonance for a rigid lattice begins to become narrower when the rate of molecular motion corresponds to the frequency span of the resonance envelope, i.e. $10^4 - 10^5$ cps.

We now consider the influence of molecular motion on T_1 . Here we are dealing with the coupling between the nuclear spins and their environment, the lattice. The atoms and molecules in the lattice exhibit thermal motion which varies in rate and amplitude with the temperature. Each proton takes part in this motion, and in so doing experiences a fluctuating magnetic field from the neighboring protons. Molecular motions occur over a wide spectrum of rates, but the motions that occur near the frequency of nuclear magnetic resonance are the ones that couple most closely with the spin system and produce the spin-lattice exchange of energy. Molecular motions occurring at higher or lower frequencies are less effective in coupling with the nuclear moments. For the fluctuating fields to be effective in producing the relaxation, it is also necessary that they be of sufficient amplitude, which means that the thermal motions must also be large enough in amplitude. Although the relaxation process has been analyzed in theoretical terms for only some selected cases that lend themselves to detailed treatment, it is apparent that the amplitudes of motion that are highly effective in spin-lattice relaxation, i.e., the amplitudes that lead to short T_1 's, must be on the scale of lattice spacings or greater.

The characteristic frequency of molecular motion is often called the *correlation frequency*, so named because even random motions tend to be correlated over short intervals of time. It is such synchronous motions that produce effective changes of energy in a variety of processes. For example, the correlation of motions is involved in the viscous flow of liquids. The inverse of the correlation frequency is the *correlation time*, τ_c . Since fluctuating magnetic fields arise in the vicinity of the proton when the molecules engage in these motions, we expect T_1 and τ_c to be related.

The theory for the dependence of T_1 upon τ_c has been treated in some detail only for simple, idealized examples. In particular, Bloembergen, Purcell, and Pound⁴ have considered the behavior of a liquid composed of molecules containing pairs of protons, e.g., water. They have examined the effect of random tumbling motion and diffusion upon the NMR relaxations. In so doing, they suppose for simplicity that all the rotational motions at a given temperature can be described by a single value of τ_c , even though it is well known that molecular motions actually involve a wide range of τ_c 's. Thus, each proton in the pair experiences a fluctuating magnetic field arising from the tumbling motion of the other proton, occurring at the single rate given by τ_c .

Figure 3 shows the predicted variation of T_1 that results when the motion consists only of rotations of the proton pairs, all with the same correlation time⁴. The theoretical dependence of T_2 upon τ_c is also shown. For our purposes, the most important feature is the minimum in T_1 that occurs when the correlation frequency is of the order of the nuclear resonance frequency. It is also seen that the simple theory predicts coincidence of T_1 and T_2 when the motion is rapid enough, i.e., when the temperature is high enough. The theory also

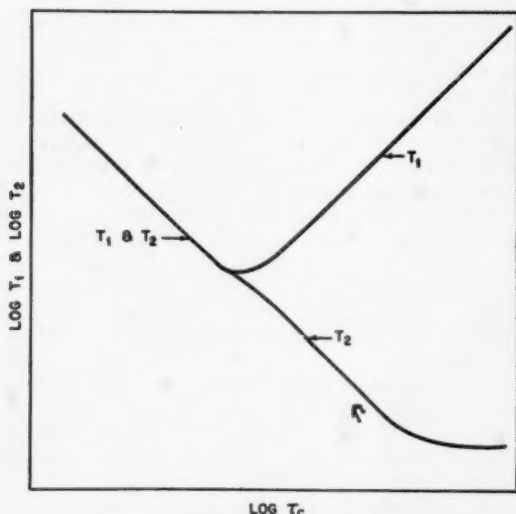


Fig. 3.—Variation of $\log T_1$ and $\log T_2$ with $\log \tau_c$, according to the theory for simple liquids (Reference 4).

predicts that in the limiting cases of $2\pi\nu_0\tau_c \ll 1$ and $2\pi\nu_0\tau_c \gg 1$, $1/T_1$ is proportional to τ_c and $1/\tau_c$, respectively. This coincidence of T_1 and T_2 is not found with complex substances, such as polymers, nor do the limiting slopes of the T_1 curve describe the correlation times in simple fashion. However, as we shall note, the existence of a minimum in the graph of T_1 versus τ_c is significant even when the motions are quite complicated.

Although the simple theory is borne out remarkably by experiment in several cases⁴, it contains some obvious shortcomings. Chief among these is the assumption that all motions at a given temperature possess the same frequency. A number of workers have sought to introduce distributions of correlation times into the treatment of dielectric and mechanical relaxation, but the task is difficult because the detailed nature of the distributions is usually unknown and because the mathematics is intractable. Corresponding problems occur when one tries to build a distribution of correlation frequencies into the theory of NMR relaxation. Accordingly, one chooses artificial distributions for the spectrum of motion which are unrealistic but mathematically convenient⁵⁻⁸. Despite the lack of realism, such models at least give qualitative information that is pertinent to actual systems.

As an example, consider that the relative population of chain segments characterized by a given correlation time, $I(\tau_c)$, is given by⁸

$$\begin{aligned} I(\tau_c) &\sim 1/\tau_c \log(b/a) \quad \text{for } b \geq \tau_c \geq a \\ I(\tau_c) &= 0 \quad \text{for } b < \tau_c \text{ and } a > \tau_c \end{aligned} \quad (8)$$

where furthermore

$$\int_0^\infty I(\tau_c) d\tau_c = 1.$$

Although this distribution is obviously artificial, it contains a variable width, defined by the ratio a/b , and it has the merit of being amenable to exact analysis. Figure 4 shows how T_1 varies with change in the span in the spectrum of motions, defined by various values of the ratio a/b . Here the abscissa is the *average* value of the correlation time in the distribution given by Equations (8). We see that an increase in the breadth of the spectrum of motions is accompanied by a broadening of the T_1 curve and by a lifting of the minimum.

Figure 4 also shows the variation of T_2 with the correlation time. As the function is graphed here, T_2 appears to be unaffected by the existence of a distribution of correlation times. However, this apparent insensitivity results

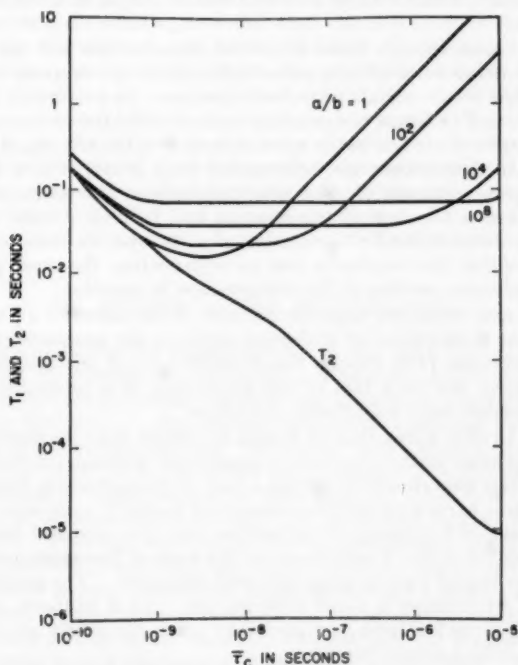


FIG. 4.—Effect of distribution in correlation frequencies upon the variation of $\log T_1$ with $\log \tau_c$ in polyethylene, as given by simple theory (Reference 6).

from the form of the distribution function and from the choice of the *average* correlation time as the variable. A different representation, using the *mean* correlation time, would display a dependence of T_2 upon the width of the distribution^{8, 9}.

We see, then, that both T_1 and T_2 relate to the molecular motion. The spin-lattice relaxation (T_1) is produced by fluctuating magnetic fields that arise from the motion. It has its greatest efficiency when the lattice frequency approximates the resonance frequency, and is influenced to a lesser degree by other lattice frequencies. The spin-spin relaxation (T_2) does not require motion, and in fact the coupling is strongest when the lattice is rigid. However,

T_2 is also affected by motion, being altered from its rigid-lattice value when the correlation frequency is great enough.

D. Motion in polymers.—It is scarcely to be expected that the theories for NMR relaxation in simple liquids, outlined above, will represent the behavior of polymers in any detail. Not only are the motions in a polymer distributed widely in frequency, but also they depart considerably from the simple form represented by Brownian rotation. An attempt has been made¹⁰ to add the effect of translation to the theory for liquids, but here again the molecules are viewed as proton pairs that possess no distribution in the spectrum of motions. Thus, it is a formidable task to develop theories that describe the NMR relaxation of complex systems such as polymer chains, and in fact this task has only been started.

However, even though these simplified theories can not be expected to apply in any detail to polymers, nevertheless there are features of the simple treatments that surely pertain to polymer studies. In particular, the existence of a minimum in T_1 at some temperature must identify the presence of a characteristic frequency of motion in the substance, approximately equal to the NMR frequency. In this respect the information from NMR is analogous to that from other measurements of molecular relaxation. For example, studies of dielectric loss as a function of temperature and frequency show distributions of correlation frequencies for the electric dipoles, and we commonly take the frequency yielding the maximum loss as representing the most probable frequency of molecular motion at the temperature in question.

We have also remarked that the breadth of the curve of T_1 versus τ_c is a measure of the distribution of molecular motions, for purposes of comparison between substances, even though the detailed form of the distribution is unknown. Indeed, the very fact of the occurrence of a minimum implies the existence of rather large amplitudes of motion.

We have already noted that T_2 begins to change from its rigid-lattice value when the molecular motions develop characteristic frequencies of about 10^6 cps. Thus, the NMR experiment identifies a pair of characteristic frequencies, one given by the line narrowing and the other given by the T_1 minimum (if it exists). A modest range of frequencies is accessible, since the resonant frequency, and hence the position of the T_1 minimum on the scale of Brownian motions, can be shifted by the use of various magnetic field strengths. For practical reasons, this range of frequencies is about 1–60 mc/sec. As it happens, not even this rather limited range has been exploited very much, for nearly all experimenters have worked with a single frequency.

E. The measurement of T_1 and T_2 .—The determination of T_2 is clear from our definition of it as the reciprocal of the line width expressed in terms of frequency. Since it is common practice to record the derivative of the resonance with respect to the magnetic field (Figure 2b), rather than the resonance itself (Figure 2a), the line width is usually taken to be the span between positive and negative peaks in the derivative curve, i.e., between points of greatest slope in the absorption envelope.

In principle, the measurement of T_1 involves heating the nuclear spin system with a strong radiofrequency field H_1 (at the resonant frequency) and observing the rate at which cooling occurs. To observe the cooling, one abruptly reduces H_1 from the high value to a low level. The initial high field saturates the spins and has the effect of reducing the intensity of the absorption signal. The subsequent low r.f. field produces essentially no heating of the spin system, and

by use of it one can observe the recovery of the absorption signal to the equilibrium value, a process which occurs with time constant T_1 . Thus, the small r.f. field may be thought of as a probe that examines the population of the lower spin state as the spin system cools down to the temperature of the lattice. Practically speaking, this method is suitable only if T_1 is long compared with the time needed to reduce H_1 and observe the recovery. Nevertheless, it illustrates what is involved in the measurement of T_1 , and in fact it has been used for some substances having long relaxation times^{4, 11, 12}.

T_1 has also been measured by the "saturation method". Here one progressively increases the strength of the radiofrequency field H_1 , producing the effect of saturation to a greater and greater extent. From Equation (7) and the accompanying discussion, we recall that the intensity of the absorption depends on the saturation factor, $(1 + \gamma^2 H_1^2 T_1 T_2)^{-1}$. From a knowledge of T_2 and H_1 , we can measure T_1 by finding the level of H_1 required to produce a given degree of saturation, e.g., such that $\gamma^2 H_1^2 T_1 T_2 = 1$. This method has been used in a number of studies on polymers, but it suffers from being rather lengthy, and it has the further disadvantage of being an indirect measurement.

A direct measurement of T_1 and T_2 involves transient methods, wherein the radiofrequency energy is applied in pulses rather than continuously. This is the method of *spin echoes*¹³⁻¹⁵. A detailed description of this pulse method is beyond the scope of this paper. Some results using this technique are cited below.

III. STUDIES OF THE RIGID LATTICE

The nature of rubberlike substances below the glass transition has only remote bearing on elastomeric properties. However, NMR studies in this temperature region are of interest because they contribute to our understanding of the array in the "lattice", and because they reveal classes of motion that are not disclosed in mechanical studies. Moreover, NMR studies often show the onset of motions involved in the transition from rigidity to elasticity.

A. Early studies.—Early studies of elastomers by NMR dealt largely with the development of motion in essentially rigid structures, as seen by changes in the line width. Features such as molecular constitution, vulcanization, reinforcement, swelling by solvents, and elongation have been investigated briefly. The studies were largely qualitative, made on isolated systems, and it would have to be conceded that in some instances they were carried out on substances too poorly characterized to be meaningful to the polymer chemist. We shall review only some salient examples of these early studies here. The reader is referred to other surveys^{2, 16} for more detailed reviews of the early work.

In one of the first studies, Holroyd and others¹⁷ showed that in unvulcanized rubber (hevea) and SBR, the NMR line width is broad and virtually independent of temperature over a wide range of low temperatures. However, they found that the resonance narrows fairly sharply at higher temperatures (somewhat above the glass transition), until at room temperature the line width approaches the narrowness found with viscous liquids.

Honnold, McCaffrey, and Mrowca¹⁸ have examined briefly the influence of molecular constitution upon the line narrowing: comparing two butadiene-acrylonitrile copolymers, one containing 26 parts of acrylonitrile and the other containing 35 parts, these authors found the latter compound to retain the rigid-lattice line width to appreciably higher temperatures than did the former. They ascribe the difference to the greater electric dipolar content of the com-

pound which is richer in acrylonitrile, suggesting that dipolar coupling tends to restrict motion.

Studies of the effect of reinforcement on the NMR spectra have been sparse. Honnold and others¹⁸ have seen almost no effect on the NMR line width of butyl rubber from the addition of carbon black, even though such reinforcement greatly changes the physical properties. These findings are in keeping with the view that reinforcement constrains the elastomer molecule only at rather widely separated points so that the chain motions seen by NMR are not much different from those in the unfilled polymer.

B. *Polyisoprenes*.—Gutowsky and his coworkers¹⁹ have compared the temperature dependence of the line width for three polyisoprenes: (a) natural poly-*cis*-isoprene (hevea), (b) synthetic poly-*cis*-isoprene (Coral rubber)²⁰, and natural poly-*trans*-isoprene (balata). Figure 5 shows the data for these three substances. The authors are unable to explain the observed differences be-

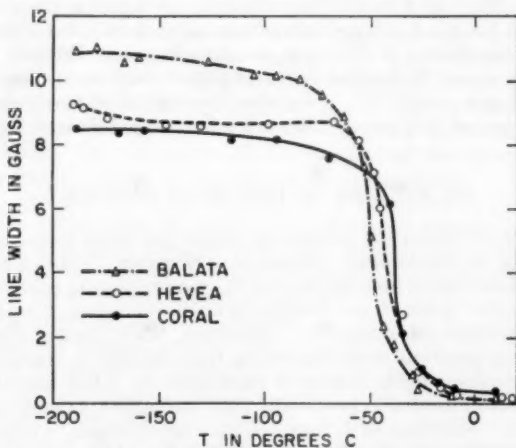


FIG. 5.—Temperature dependence of the NMR line width for unvulcanised hevea rubber, Coral rubber, and balata (Reference 19).

tween the two *cis* polymers, which are closely similar according to other kinds of measurement²⁰. Possibly the differences seen in NMR come from disparities in the molecular weight distributions. One might conjecture that the hevea contained a low molecular weight component that acted as a plasticizer. The *trans* form crystallizes much more readily than the *cis* form²¹. It is seen that the line width at low temperature is distinctly greater for balata than for the *cis* isomer, in keeping with the closer chain packing that the *trans* isomer possesses on the average, from its crystallinity.

The narrowing of the resonance occurs in about the same temperature range for the three compounds. Evidently the narrowing is related to the glass transition. In dilatometric studies of hevea²², the glass temperature occurs at about -73°C . The narrowing shown in Figure 5 at about -50°C probably relates to the same relaxation processes. The writer is unaware of measurements of the transition in balata by other methods. In any case, this narrowing

is certainly not related to the melting of crystallites, for the melting of the two polymorphs of the *trans* isomer occurs well above room temperature²³. The crystalline regions would be expected to yield a broad resonance envelope, until the temperature is raised to the point at which melting occurs to an appreciable extent. Indeed, with several partly crystalline polymers, one can distinguish a broad envelope superimposed on a narrow envelope^{24, 25}. The former represents the immobile constituents, which ordinarily belong to the crystalline regions, while the latter represents the mobile segments, which are presumed to occur mainly in the amorphous regions. However, when both a broad and a narrow resonance occur, the adjustment of the NMR apparatus to view the resonance in an undistorted fashion results in a loss of intensity in the broad component. Therefore, in such circumstances the broad component is detectable only if it is rather intense. Gutowsky and his coworkers do not report the existence of a broad component at temperatures above the line narrowing (Figure 5). From this we conclude that the balata must have contained a

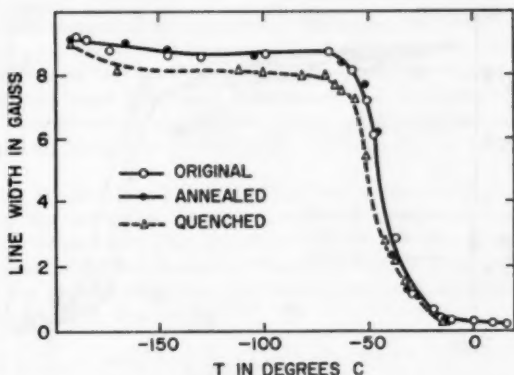


Fig. 6.—Temperature dependence of NMR line width in hevea rubber as originally received, following quenching, and following an annealing treatment (Reference 19).

rather large proportion of mobile segments, so that the resonance failed to reveal the broad (crystalline) component at the higher temperatures. A large content of low molecular weight constituents would contribute to such mobility.

Gutowsky and his colleagues¹⁹ have also examined the temperature dependence of the line width in an uncured sample of hevea which had been subjected to thermal treatments designed to change the degree of crystallinity. Figure 6 shows their data for (a) the compound as originally received; (b) a quenched sample, which had been heated to 60°C for 4 hours and then quickly cooled by liquid nitrogen; (c) an "annealed" sample, made by warming the quenched sample to room temperature for a day and then chilling it to -14°C for 4 hours. It is seen that the quenched sample exhibits a narrower resonance at low temperature than the original material. This difference implies that the chains have become less closely packed on the average, which is what one would expect from the thermal treatment. Also, the resonance narrows at lower temperatures than in the comparison samples, demonstrating that the constraints to chain motion are smaller than in the original material.

It is seen in Figure 6 that the "annealed" material behaves about the same as the original sample. This similarity is not surprising, in view of what is known of the crystallization behavior of rubber. Even under optimum conditions, natural rubber crystallizes slowly^{26, 27}, and the ultimate degree of crystallinity is low compared with that found in many other crystallizable polymers. Thus it seems likely that the "annealing" used by Gutowsky and coworkers yielded a material that differed little in crystalline content from the original material. It would be interesting to examine the NMR spectrum of rubber that had been relatively well crystallized, e.g., "stark" rubber.

Gutowsky and his colleagues¹⁹ have also studied the effect of vulcanization upon molecular motion. Figure 7 shows the temperature dependence of line width in three samples of vulcanized hevea, made from the same mix and cured for different intervals. The composition for these samples corresponds to a semihard rubber (20 parts of sulfur, 0.5 parts of mercaptobenzothiazole as an accelerator, and 6 parts of zinc oxide as an activator). It is seen that an in-

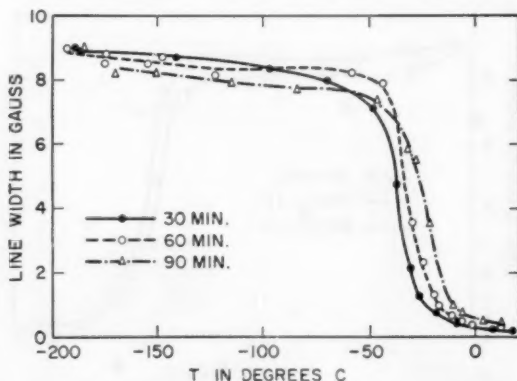


Fig. 7.—Temperature dependence of the NMR line width in three samples of semi-hard vulcanized rubber, cured for different intervals (Reference 19).

crease in the time of curing shifts the NMR narrowing to higher temperatures, i.e., increases the constraints to chain motion.

However, the effect of vulcanization upon the NMR narrowing is complex, as Gutowsky and his coworkers point out. Although these studies indicate a trend toward higher transition temperatures with increased time of curing and with increased amounts of combined sulfur, the development of chain mobility is also found to depend on the amount of raw sulfur used in the mixes. The authors suggest that one important variable is the degree of crystallinity. They conclude that one effect of vulcanization is a reduction in the crystallinity. They base this view upon the observation that the development of chain mobility, as seen from the narrowing of the resonance, occurs at a somewhat higher temperature in uncured hevea than in vulcanizates with low contents of bound sulfur. They suggest that this trend occurs because the constraints to chain motion introduced by crosslinking are more than offset by the lessening of the constraints imposed by the crystalline regions. Thus, the effect of vulcanization in reducing the over-all mobility is thought to become important

only at higher sulfur content, when crosslinking prevails in constraining segmental mobility despite the accompanying loss in crystallinity.

These conclusions from the NMR studies cannot be regarded as settled. In the first place, the differences seen in these studies may have come from subsidiary effects in the vulcanization such as the degradation of the hydrocarbon, rather than from a loss in crystallinity. The products of degradation would be expected to be relatively mobile, and their presence would depress the temperature of NMR narrowing, until the degree of crosslinking is made high enough to impose a net loss in segmental motion. Moreover, the view that mild curing affects crystallinity is in some conflict with results from other studies. For example, Bekkedahl and Wood²⁸ found that the degree of crystallinity, as seen from the specific volume, depends little upon the extent of vulcanization at low sulfur content. However, these authors dealt with rather low amounts of combined sulfur. It is reasonable to expect that the content of combined sulfur will affect the degree of crystallinity at some level. The ramifications of these variables with respect to segmental mobility deserve further study.

C. The second moment of the resonance.—We have already remarked that the resonance envelope for a rigid lattice consists of a superposition of a great many individual resonances. If we have a model for the lattice structure, we can in principle calculate these individual resonances, and can therefore predict the shape of the resonance envelope, for comparison with experiment. In practice, however, this calculation is prohibitively difficult for all but the simplest structures.

Instead of this difficult calculation of the local fields and their contributions to the shape of the resonance, we may calculate a simpler quantity, the *second moment* of the resonance. This quantity is given by Van Vleck's²⁹ rigorous quantum mechanical determination of the mean square local field in the rigid lattice. For the proton resonance, the second moment, expressed in units of magnetic field strength, is given by

$$\Delta H_2^2 = C \sum_{i>j} (3\cos^2\theta_{ij} - 1)^2 r_{ij}^{-6} \quad (9)$$

$$C = \frac{1}{3} I(I+1) \gamma^2 (\hbar/2\pi)^2$$

Here r_{ij} is the distance between protons i and j , and θ_{ij} is the angle between the vector \mathbf{r}_{ij} and the direction of the field applied by the laboratory magnet. I is the nuclear spin ($=\frac{1}{2}$ for the proton). Note that the factor C contains only numerical terms and constants of nature. In evaluating Equation (9), we consider a typical nucleus in the postulated structure and determine the distances and angles to all the other nuclei in the lattice. Because the radial term falls off so rapidly, it turns out that only comparatively close neighbors make significant contributions to the summation.

Equation (9) implicitly presumes that each proton is structurally equivalent to every other proton, as is virtually the case, for example, in linear polyethylene of very high molecular weight. However, the rubber molecule has three kinds of protons corresponding to the CH_3 , CH_2 , and CH groups in the isoprene unit $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$. When there are structurally different protons in the lattice, we do a separate summation for each type and combine these sums with appropriate weighting factors. For unoriented polymers, the angle θ_{ij} takes on all values, and the term $(3\cos^2\theta_{ij} - 1)^2$ averages to the value $\frac{8}{5}$. It should be noted that r_{ij} involves not only the distances within a given mole-

cule, but also the separations between molecules. For noncrystalline substances such as rubber, we have to be content with estimated values for the intermolecular terms.

Having postulated a structure, we can therefore arrive at a calculated value of the second moment, for comparison with experiment. The experimental value is found by measuring the resonance envelope and determining the second moment of the figure about the point $H = H_0$, in a manner that is entirely equivalent to the determination of moments in mechanics:

$$\Delta H_2^2 = \frac{\int_{-\infty}^{\infty} (H - H_0)^2 \cdot f(H) dH}{\int_{-\infty}^{\infty} f(H) dH} \quad (10)$$

Here $f(H)$ is the amplitude of the absorption at field strength H . Even if $f(H)$ is not a convenient analytic function, Equation (10) can still be evaluated from the experimental data by numerical methods. As we have already remarked, it is customary to measure $\partial f(H)/\partial H$, rather than $f(H)$, but this difference is handled in the integration. By comparing the results of calculation and experiment, we may test the merit of the postulated structure.

Molecular motion has an important effect on the second moment. The angular term in Equation (9) takes on some average value, depending upon the values of θ_{ij} that arise from the motion. Furthermore, the distances r_{ij} between protons on neighboring molecules will vary in a complicated way as a result of the motion, and will have to be represented by some sort of average, which usually can be found only by estimate. Such an average also applies to the r_{ij} 's within a molecule when different parts of the same molecule move with respect to each other. Thus, the rotation of the methyl group in the isoprene unit of the rubber molecule does not affect the magnitude of the r_{ij} 's within the group, but alters the distances to protons elsewhere in the molecule. Changes in the second moment for some examples of torsional and rotational motion have been calculated in some detail²⁰⁻²².

It should be mentioned that there is some objection to the foregoing extension of Equation (10) to describe motion¹. From quantum mechanical theory, the value of the second moment should be invariant with respect to such motions. However, from arguments that are beyond the scope of this review, it has been shown^{23, 24} that the second moment in the presence of these motions consists of two parts. One portion is affected by motion in a manner that can be calculated as outlined in the preceding paragraph. The other portion corresponds to the development of widely-spread wings in the resonance envelope, which have intensities that are ordinarily too faint to be seen. Although these combined terms equal the rigid-lattice value, in practice it is only the former component that is measured in the presence of rapid motion. However, in the region of transition from a broad to a narrowed resonance, these wings in the resonance envelope may in fact be measurable, depending upon the performance of the spectrometer. Therefore, one should be suspicious of values of the second moment observed over the transition temperatures. These values have doubtful meaning, since they may reflect the signal-to-noise characteristics of the apparatus, rather than the state of motion in the sample. However, when the measured second moment attains a plateau over a range of temperatures, one may probably assume that the ambiguous fringes of the resonance have

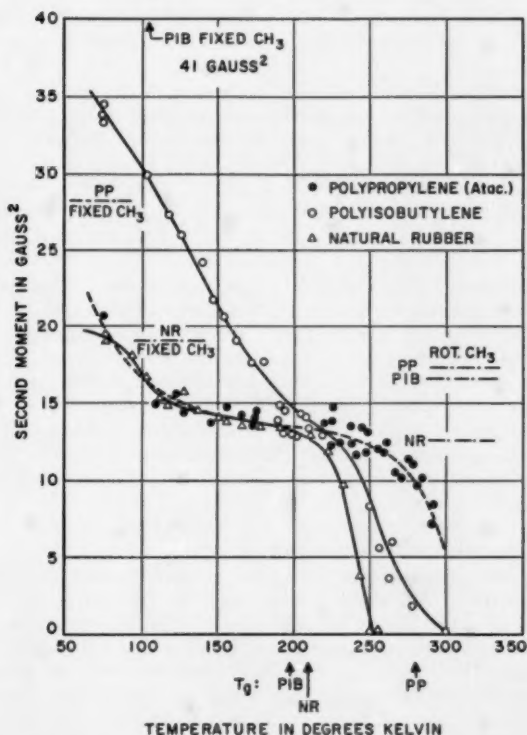


Fig. 8.—Temperature dependence of the second moment of the resonance, for hevea rubber, atactic polypropylene, and polyisobutylene (Reference 35).

effectively vanished, and that the observed value describes fairly the state of motion^{33, 34}.

Figure 8 shows the second moment for three elastomers^{35, 36}: (a) unvulcanized hevea; (b) polyisobutylene, $\bar{M}_n \cong 1 \times 10^6$; (c) atactic polypropylene. These three compounds afford interesting comparisons, for they are all hydrocarbons with methyl-substituted chains. Several features in Figure 8 are noteworthy. In the first place, we note that the compounds differ markedly in their low-temperature behavior. With hevea, the second moment appears to approach a plateau as the temperature falls. This trend suggests that the molecular motion becomes quenched with approach to the liquid nitrogen temperature. With polypropylene and polyisobutylene, on the other hand, the second moment shows no sign of a plateau at low temperatures. Even though the values are somewhat ambiguous in this transition region, the fact that a plateau fails to develop is evidence that motion persists even at the liquid nitrogen temperature.

With both hevea and polypropylene, the second moment is seen to narrow to a plateau which occurs in a temperature interval centered near 175° K. There is an inflection in the curve for polyisobutylene, suggestive of a plateau,

at about this same temperature. Moreover, there is a further marked decrease in the second moment for each compound somewhat above the respective glass temperatures.

Gutowsky and his colleagues^{19, 37} have suggested that rubber exhibits rotation of the methyl groups about the threefold axis at low temperatures. They make this assignment by analogy with the behavior of some methyl-substituted methanes, which have been shown³⁸ to develop this kind of motion near 120° K. This is a plausible interpretation for the low-temperature motions shown in Figure 8 for all three polymers, since rotation of the methyl group about its symmetry axis would be expected to involve relatively little hindrance and therefore should be active at low temperatures.

One can supplement these views by some calculations. Powles³⁹ has calculated the second moment for polyisobutylene, using structural data from x-ray diffraction studies⁴⁰ of the stretched polymer, which is crystalline. Unoriented polyisobutylene crystallizes with great difficulty⁴¹, but the second moment that pertains to it should not be very much less than for the oriented form. One may make this conclusion because the chief contributions to the second moment come from the methyl groups, involving large interactions from the triads of protons and large couplings between the closely-spaced methyl groups on successive chain elements³⁹. The value calculated for the rigid lattice is plotted in Figure 8, as is the value calculated assuming that all of the methyl groups are rotating about the threefold axis³⁹. It is seen that the latter figure is close to the inflection point in the experimental curve.

Similarly, the rigid-lattice value of the second moment for polypropylene has been calculated⁴² from data on the crystalline (isotactic) form of the compound, and is shown in Figure 8. The value for hevea comes from a weighted sum of the second moments due to the CH₃, CH₂, and CH groups, augmented by an amount estimated to account for interactions between groups and between molecules^{36, 37}. The calculated second moments are also shown for hevea and polypropylene in which there is motion consisting solely of rotation of all the methyl groups at an effective rate.

From a comparison between calculation and experiment, we see that hevea may be regarded as motionless at the liquid nitrogen temperature, and that it develops rotation in all its methyl groups near 120° K. Furthermore, it develops still greater motion, presumably involving the chain segments, at temperatures above about 220° K. On the other hand, polypropylene evidently retains motion at the lowest temperatures studied. The second moment narrows to a plateau at about 150° K, with a magnitude that agrees well with the value calculated for methyl rotation. We may therefore conclude that it is this motion which persists in some degree down to 77° K. Above 250° K this polymer, too, shows a further decrease in the second moment that can be ascribed to motion of the chain segments. With polyisobutylene, however, the second moment does not fall to the value calculated for methyl rotation until the temperature is quite high, about 200° K. There is no clear-cut separation of one mode of motion from another, for apart from the inflection that we mentioned above, the curve falls continuously over a wide temperature range. It appears that motion of the methyl groups does not become effective, in terms of the rates that are important to NMR narrowing, until motion of the main chains has also begun. Indeed, Powles³⁹ has concluded that the methyl groups are interlocked with one another because of their closeness and that motion of the main chain is required before the methyl groups can be freed.

IV. STUDIES OF THE RUBBERY STATE

A. *Natural rubber*.—As we have seen, the narrowing of the resonance from the rigid lattice value occurs some 10–20 degrees above the glass transitions recorded by dilatometry. Thus, the line width (T_2) transition comes near the onset of rubbery behavior. From the earlier discussion, we expect T_1 measurements to be sensitive to correlation motions that are characteristic of higher temperatures. NMR measurements are therefore applicable to the rubbery state and to study of the important changes that occur when the glasslike state develops.

Figure 9 shows the temperature dependence of T_1 for natural rubber, from the studies of Gutowsky and his coworkers¹⁹. The spin-lattice relaxation was measured by a pulse technique, using two different radio frequencies. Figure 9 shows data for an uncured sample and for a vulcanized specimen, the latter having been cured for 60 minutes at 287° F from a mix containing 20 parts of sulfur, 0.5 parts of mercaptobenzothiazole as an accelerator, and 6 parts of

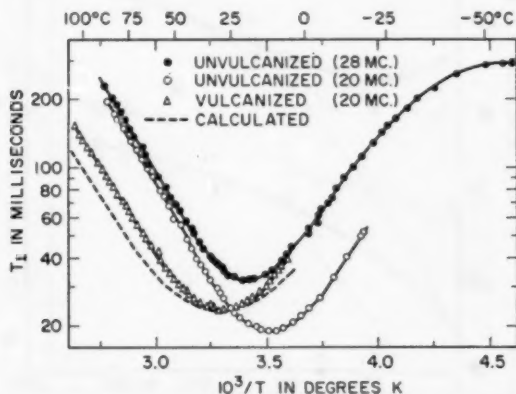


Fig. 9.—Variation of the spin-lattice relaxation time with the reciprocal of the absolute temperature, for hevea rubber (Reference 19).

zinc oxide as an activator. The reciprocal of the absolute temperature is used for the abscissa. This choice is made because the molecular motions can be expected to have a temperature dependence that is given fairly satisfactorily by an Arrhenius expression: $\tau_c = \tau_c^0 \exp(\Delta E/RT)$. Thus, the abscissa may be taken to represent the correlation time on some logarithmic scale.

There are several important features in the data of Figure 9. In the first place, it is seen that the T_1 curves have minima, indicating the presence of large-amplitude motions in abundance near the NMR frequency. Furthermore, the T_1 minimum shifts toward higher temperature, i.e., toward shorter correlation times, as the resonant frequency is raised, a trend which is in keeping with the theory for simple liquids⁴. Also, the value of T_1 at the minimum increases with increase in the resonant frequency, a trend which is also expected from the theory for simple liquids. Finally, we note that vulcanization displaces the minimum to higher temperatures. This effect is likewise what we

would expect, for presumably vulcanization constrains the chain motion, so that the frequencies characteristic of the T_1 minimum develop only at higher temperatures.

Thus, the temperature dependence of T_1 in rubber follows qualitatively the pattern predicted by the theory developed for simple liquids⁴. It is not surprising, however, that there are discrepancies. In the first place, although the T_1 minimum shifts in the predicted direction with change in the resonant frequency, the shift is greater than that given by the simple theory. The frequencies of resonance, 20 mc/sec and 28 mc/sec, stand in the ratio 1:40. If the T_1 minimum represents a characteristic correlation time which depends on temperature according to the Arrhenius relation, the position of the minimum along the axis of reciprocal temperature should shift by this same factor. Instead, in the two curves for unvulcanized rubber, the position of the minimum is ob-

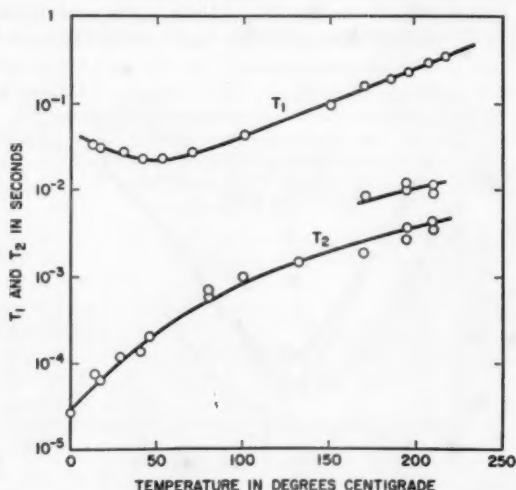


Fig. 10.—Temperature dependence of T_1 and T_2 in polyisobutylene (Reference 7).

served to shift by the factor 1.63. In addition, the magnitude of T_1 at the minimum, according to the simple theory⁴, should be proportional to ν_0 . However, the observed T_1 's at the minima of the two curves for unvulcanized rubber stand in the ratio 1:74.

The T_1 curves in Figure 9 resemble in shape the function given by the theory for simple motion in liquids (cf. Figure 3). Gutowsky and his coworkers¹⁹ were therefore led to calculate the temperature dependence of T_1 for the unvulcanized sample in terms of this theory. To do this, they took the observed limiting slope at high temperature to define an activation energy in the Arrhenius expression for correlation time, and fitting the calculated spin-lattice relaxation to the observed curve at the T_1 minimum, they plotted the calculated T_1 dependence on the scale of reciprocal temperature (dashed line in Figure 9). We note that this computed curve is flatter than the the experimental curve. However, as Gutowsky points out¹⁹, one would expect the opposite situation

to occur as a consequence of the presence of a distribution of relaxation times (cf. Figure 4). Gutowsky and his coworkers suggest that this discrepancy between theory and experiment may be due to a serious departure from the Arrhenius law, or to the existence of an unexpectedly narrow distribution in the correlation frequencies, perhaps caused by the presence of cooperative motions. As we shall remark later, there is wide evidence for departure from the Arrhenius relation at temperatures not far above the glass temperature. However, it seems likely that the disparities just mentioned come instead from the inadequacies of the theory in describing the motions of the polymer. As we have noted, the theory⁴ relates to molecules composed of proton pairs which are engaged only in Brownian rotations, all at the same rate. The experiments

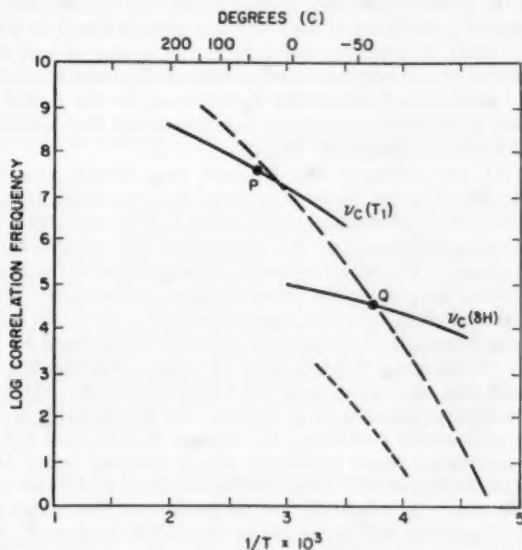


Fig. 11.—Comparison of temperature dependence of correlation times found in mechanical and dielectric measurements (dashed curves) with those found by NMR (solid curves) in studies of polyisobutylene (Reference 7).

pertain to much more complicated arrays of protons, attached to molecules that are engaged in a complex set of motions involving both substituents and main chains, and exhibiting a wide spectrum of relaxation times. It would therefore be merely fortuitous if the behavior of rubber could be described in detail by the simple theory. However, it should be reiterated that the qualitative features of the theory, particularly the significance of the T_1 minimum in identifying a characteristic motion in the sample, retain their meaning when applied to complex systems.

B. Polyisobutylene.—Similar behavior is seen in studies of polyisobutylene. Figure 10 shows the variation of T_1 and T_2 with temperature, from the work of Powles and Luszczynski⁷. A minimum in T_1 occurs at about 50° C, with a

proton resonance frequency of 21.5 mc/sec. These authors also call attention to the differences between their data and the simple theory, particularly in the behavior of T_1 and T_2 at the higher temperatures. The theory predicts that T_1 and T_2 will approach each other when the correlation time is sufficiently short, i.e., at high temperatures. Also, the theory predicts that the ratio T_1/T_2 will be 2.25 at the temperature of the T_1 minimum (cf. Figure 3). In polyisobutylene this ratio is found to be 73. Moreover, no trend toward convergence of T_1 and T_2 is noted even at rather high temperatures.

Powles and Luszczyński⁷ have compared their NMR relaxation data with some mechanical and dielectric data reported in the literature for this polymer⁴³⁻⁴⁷. Figure 11 gives a composite of these data. The mechanical and dielectric relaxations (dashed lines) are shown in simplified form². Over certain temperatures the mechanical losses appear in two different regions of the spectrum⁴⁶, although the existence of only one loss zone is found in some studies⁴⁴. It is not clear what mechanisms are involved in a pair of loss regions. However, the existence of two separate mechanisms at the same temperature would account for the large ratio T_1/T_2 at the T_1 minimum, for the T_1 and T_2 processes may be ascribed to separate correlation motions, rather than the single correlation motion inherent in the simple theory⁴.

In Figure 11, the points P and Q show, respectively, the characteristic frequencies identified by the T_1 minimum and the line width transition. The solid curves give the approximate variation of ν_c with temperature, predicted from simple treatments⁴ based on the assumption of a single correlation time at each temperature. The introduction of a distribution of frequencies has the qualitative effect of improving the correspondence between the NMR data and the mechanical and dielectric loss measurements⁷. Even though it has not been practical to determine the frequency distributions in detail for real polymer systems, their effects are predicted from the model represented in Figure 4. The effects may also be explained in the following terms. With a given distribution of molecular motions in a sample, the effectiveness of molecules in producing the spin-lattice relaxation will depend in part upon the rate of their motion. In particular, those molecules whose motions occur at nearly the frequency of the resonance will be more effective than molecules having higher or lower frequencies. At relatively low temperatures, the center of gravity of the spectrum of motions will occur below the NMR frequency, and only the molecules with frequencies at the upper end of the spectrum will be highly effective in causing the T_1 relaxation. Conversely, at relatively high temperatures the molecules with frequencies in the low end of the spectrum will be the most effective. In terms of Figure 11, the result of considering frequency distributions will be to increase the slope of the solid curve through P . A similar result will pertain to the curve through Q describing the temperature dependence of T_2 .

C. Effects of pressure.—Measurements of molecular relaxation at elevated pressure are important because they have to do with the relation between molecular mobility and free volume. The concept of free volume, although not too well defined in an operational sense, has been helpful in the use of specific volume measurements to describe molecular mobility, particularly in the temperature region near the glass transition⁴⁸. From the free volume interpretation of viscoelastic properties and their temperature dependence, it follows that the application of hydrostatic pressure should constrain the molecular mobility. NMR measurements appear to be highly promising for the study of the free

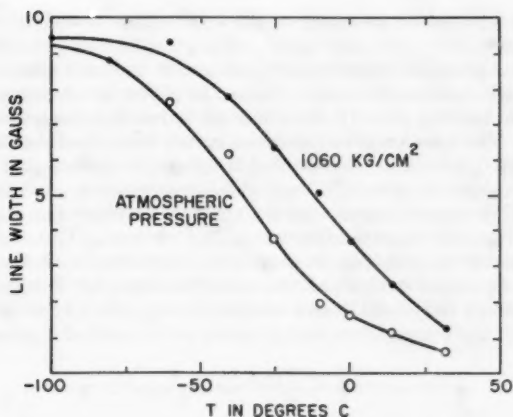


FIG. 12.—Line width as a function of temperature in polyisobutylene, measured at two different pressures (Reference 5).

volume concept in relation to mobility. Unfortunately, not much work has been done with NMR at elevated pressures.

Nolle and Billings⁵ have examined the NMR relaxation in polyisobutylene at pressures up to about 1000 atm and at various temperatures. Figure 12 shows the temperature dependence of the proton line width in polyisobutylene ($\bar{M}_v = 1.35 \times 10^6$), measured at atmospheric pressure and at a pressure of 1060 kg/cm² (1020 atm). It is seen that the application of hydrostatic pressure causes the line narrowing to occur at higher temperatures. As an approximation, it may be said that the effect of pressure upon the resonance is to displace the NMR transition along the temperature axis (Figure 13). That is to say,

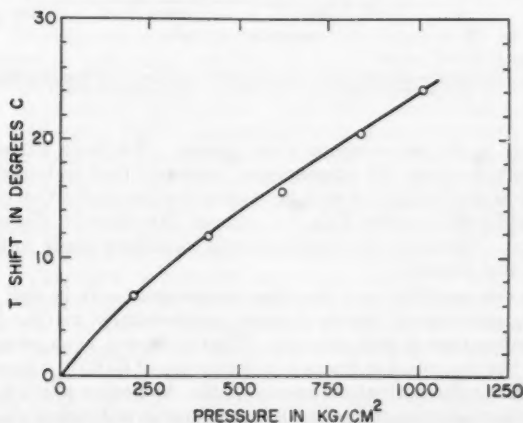


FIG. 13.—Effect of hydrostatic pressure upon the temperature at which the line width in polyisobutylene is half its rigid-lattice value (Reference 5).

an increase in hydrostatic pressure causes a reduction in molecular motion, as one would expect.

The effect of pressure in constraining molecular motion is also seen in studies of the spin-lattice relaxation time. Figure 14 shows the pressure dependence of T_1 , expressed as the ratio of the value at elevated pressure to that at one atmosphere. The data are given as ratios rather than absolute values because of experimental difficulties. We see that the pressure coefficient of T_1 decreases as the temperature is raised. The highest temperature used by Nolle and Billings, 65° C, is approximately the temperature at which one would expect a minimum in T_1 at the resonant frequency, 28.8 mc/sec. This relative insensitivity of T_1 at 65° to a change in pressure is consistent with the view that a minimum in T_1 occurs here at atmospheric pressure, for if temperature and pressure are nearly reciprocal to one another in their effect upon the correlation spectrum, both the temperature and pressure coefficients of T_1 should approxi-

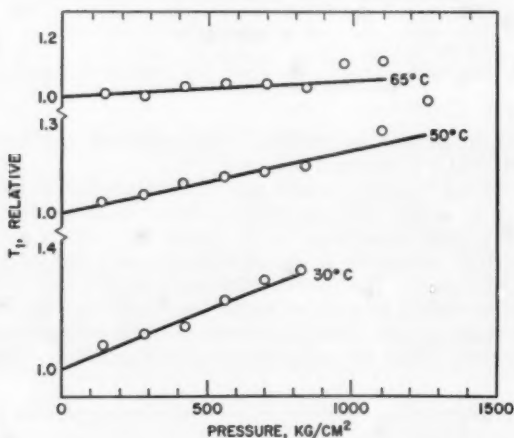


FIG. 14.—Spin-lattice relaxation time in polyisobutylene, as a function of pressure and temperature, relative to its value at 1 atm (Reference 5).

mately vanish in the same temperature region. We have already seen that still higher temperatures (at atmospheric pressure) lead to longer T_1 's. One would therefore predict that at such temperatures the application of hydrostatic pressure would yield shorter T_1 's, i.e., curves like those in Figure 14 having negative slope. However, no measurements have been made in this region of temperature and pressure.

D. *Molecular mobility near the glass temperature.*—It is well known that viscoelastic properties of liquids depend exponentially on the temperature, when the temperature is high enough. That is to say, such properties as the viscosity may be described in terms of a factor $\exp(\Delta E/RT)$, where ΔE is formally equivalent to the activation energy in the Arrhenius relation. However, the viscoelastic properties of liquids that are capable of forming glasses undergo major changes in the vicinity of a characteristic temperature. This is the glass temperature, T_g , to which we have already referred somewhat obliquely.

It is an important observation that the temperature dependence of molecular relaxations departs markedly from the Arrhenius form within a temperature range somewhat above T_g . We have already noted, in the discussion of the temperature dependence of T_1 for natural rubber (Figure 9), that disparities occur between experiment and simple theory. One suggested source for the inadequacy of the theory was the unsuitability of the Arrhenius relation. We shall amplify this point in the following discussion.

In studies of viscoelasticity, it has been observed that the properties of many glass-forming substances, both polymeric and monomeric, can be expressed in terms of a parameter $a_T(T)$, the ratio of the relaxation time at temperature T to that at a reference temperature⁴⁹. The temperature dependence of a_T , in the region of transition from glasslike to rubberlike properties, is given quite satisfactorily by what is commonly called the WLF equation⁵⁰, which may be written in the form

$$\log a_T = \frac{-c_1(T - T_g)}{c_2 + T - T_g} \quad (11)$$

$$T - T_g \lesssim 100^\circ \text{C}$$

This expression is plainly very different from the Arrhenius expression as a description of the molecular relaxations. T_g is taken as a reference temperature, and the coefficients c_1 and c_2 are found empirically^{50, 51}. Although the WLF equation is empirical, its universality suggests strongly that it is based on fundamental considerations. Theoretical models have been developed^{50, 52, 53} which view the molecular behavior near the glass temperature as a process in which extensive cooperative movement occurs among segments of neighboring molecules. These models lead to expressions of the WLF form at temperatures not far above T_g and to the Arrhenius form at high temperatures. Indeed, Ferry and his coworkers⁵⁴ have reported instances of multiple relaxation mechanisms, exhibited by molecules with substituent groups, which appear to show simultaneously the WLF dependence for the motion of the main chains and the Arrhenius dependence for the motion of the substituents.

Since the WLF description of the temperature dependence of viscoelastic properties relates to molecular mobility, it would seem fruitful to carry out parallel investigations by NMR. However, the NMR data obtained so far offer virtually no pertinent information, apart from corroborative data of the sort shown in Figure 11. NMR measurements have not been carried out with a view of enlarging upon the concepts inherent in the WLF treatment. To determine the applicability of a reduction function of the form $a_T(T)$, we need a series of isotherms, each covering a wide enough frequency range to allow the relaxation functions to be characterized. Instead, nearly all NMR measurements have been carried out at some constant frequency, ν_0 , over a range of temperatures. Therefore, a different approach should be tried with NMR studies on elastomers, involving isotherms taken over a range of frequencies. One should be realistic about the limitations of the method, since the experiments will be restricted by the frequency range that is readily available, 2–60 mc/sec, and still more by the complexities of interpreting NMR relaxations in terms of molecular mobility. On the other hand, the use of pressure as a variable is not too difficult in NMR. Despite the limitations of the method, it is fair to expect NMR to provide considerable new information on the molecular behavior of elastomers.

V. REFERENCES

- ¹ Pake, G. E., in "Solid State Physics", Vol. 2, pp. 1-92, edited by F. Seitz and D. Turnbull, Academic Press, Inc., New York, 1956.
- ² Powles, J. G., *Polymer* **1**, 219 (1960).
- ³ Slichter, C. P., *Ann. N. Y. Acad. Sci.* **70**, 769 (1958).
- ⁴ Bloembergen, N., Purcell, E. M. and Pound, R. V., *Phys. Rev.* **73**, 679 (1948).
- ⁵ Nolle, A. W. and Billings, J. J., *J. Chem. Phys.* **30**, 84 (1959).
- ⁶ McCall, D. W., Douglass, D. C. and Anderson, E. W., *J. Chem. Phys.* **30**, 1272 (1959).
- ⁷ Powles, J. G. and Luszczynski, K., *Physica* **25**, 455 (1959).
- ⁸ Luszczynski, K. and Powles, J. G., *Proc. Phys. Soc. London* **74**, 408 (1959).
- ⁹ Powles, J. G., paper presented at the Symposium on Macromolecules, International Union of Pure and Applied Chemistry, Wiesbaden, Germany, October, 1959.
- ¹⁰ Skrotalski, G. V. and Kokin, A. A., *J. Exp. Theor. Phys. (USSR)* **36**, 481 (1959).
- ¹¹ Drain, D. E., *Proc. Phys. Soc. London* **62A**, 301 (1949).
- ¹² Anderson, W. A. and Arnold, J. T., *Phys. Rev.* **101**, 511 (1956).
- ¹³ Hahn, E. L., *Phys. Rev.* **80**, 580 (1950).
- ¹⁴ Hahn, E. L., *Physics Today* **6**, 4 (1953).
- ¹⁵ Carr, H. Y. and Purcell, E. M., *Phys. Rev.* **94**, 630 (1954).
- ¹⁶ Slichter, W. P., *Fortschr. Hochpolym.-Forsch.* **1**, 35 (1958).
- ¹⁷ Holroyd, L. V., Codrington, R. S., Mrowca, B. A. and Guth, E., *J. Appl. Phys.* **22**, 696 (1951); *RUBBER CHEM. & TECHNOL.* **25**, 767 (1952).
- ¹⁸ Honnold, V. R., McCaffrey, F. and Mrowca, B. A., *J. Appl. Phys.* **25**, 1219 (1954); *RUBBER CHEM. & TECHNOL.* **28**, 480 (1955).
- ¹⁹ Gutowsky, H. S., Saika, A., Takeda, M. and Woessner, D. E., *J. Chem. Phys.* **27**, 534 (1957).
- ²⁰ Stavely, F. M. and others, *Ind. Eng. Chem.* **48**, 778 (1956); *RUBBER CHEM. & TECHNOL.* **29**, 673 (1956).
- ²¹ Goppel, J. M. and Ariman, J. J., *Appl. Sci. Research A1*, 422 (1949); *RUBBER CHEM. & TECHNOL.* **23**, 310 (1950).
- ²² Bekkedahl, N., *J. Research Natl. Bur. Standards* **13**, 411 (1934); *RUBBER CHEM. & TECHNOL.* **8**, 5 (1935).
- ²³ Mandelkern, L., Quinn, F. A., Jr. and Roberts, D. E., *J. Am. Chem. Soc.* **78**, 926 (1956); *RUBBER CHEM. & TECHNOL.* **29**, 1181 (1956).
- ²⁴ Wilson, C. W., III and Pake, G. E., *J. Polymer Sci.* **10**, 503 (1953); *J. Chem. Phys.* **27**, 115 (1957).
- ²⁵ Slichter, W. P. and McCall, D. W., *J. Polymer Sci.* **25**, 230 (1957).
- ²⁶ Wood, L. A., in "Advances in Colloid Science", Vol. II, pp. 58-93, edited by H. Mark and G. S. Whitby, Interscience Publishers, Inc., New York, 1946.
- ²⁷ Roberts, D. E. and Mandelkern, L., *J. Am. Chem. Soc.* **77**, 781 (1955); *RUBBER CHEM. & TECHNOL.* **28**, 718 (1955).
- ²⁸ Bekkedahl, N. and Wood, L. A., *J. Chem. Phys.* **9**, 193 (1941); *RUBBER CHEM. & TECHNOL.* **14**, 544 (1941).
- ²⁹ Van Vleck, J. H., *Phys. Rev.* **74**, 1168 (1948).
- ³⁰ Andrew, E. R. and Bersohn, R., *J. Chem. Phys.* **18**, 159 (1950).
- ³¹ Andrew, E. R., *J. Chem. Phys.* **18**, 607 (1950).
- ³² Gutowsky, H. S. and Fack, G. E., *J. Chem. Phys.* **18**, 163 (1950).
- ³³ Andrew, E. R. and Newing, R. A., *Proc. Phys. Soc. London* **B72**, 959 (1958).
- ³⁴ Abragam, A., "The Principles of Nuclear Magnetism", The Clarendon Press, Oxford, 1960, p. 451 ff.
- ³⁵ Slichter, W. P., *Makromol. Chem.* **34**, 67 (1959).
- ³⁶ Slichter, W. P., *Ann. N. Y. Acad. Sci.* **83**, 60 (1959).
- ³⁷ Gutowsky, H. S. and Meyer, L., *J. Chem. Phys.* **21**, 2122 (1953).
- ³⁸ Gutowsky, H. S. and Powles, J. G., *J. Chem. Phys.* **21**, 1695 (1953).
- ³⁹ Powles, J. G., *Proc. Phys. Soc. London* **B69**, 281 (1956).
- ⁴⁰ Liquori, A. M., *Acta Cryst.* **8**, 345 (1955).
- ⁴¹ Kell, R. M., Bennett, B. and Stickney, P. B., *RUBBER CHEM. & TECHNOL.* **31**, 499 (1958).
- ⁴² Slichter, W. P. and Mandell, E. R., *J. Appl. Phys.* **29**, 1438 (1958).
- ⁴³ Thomas, P. A. and Robinson, D. W., *Brit. J. Appl. Phys.* **6**, 41 (1955).
- ⁴⁴ Kabin, S. P. and Mikhailov, G. P., *Soviet Physics—Tech. Phys.* **1**, 493 (1957).
- ⁴⁵ Fitzgerald, E. R., Grandino, L. D. and Ferry, J. D., *J. Appl. Phys.* **24**, 650 (1953).
- ⁴⁶ Schmieder, K. and Wolf, K., *Kolloid Z.* **134**, 149 (1953).
- ⁴⁷ Fox, T. G. and Flory, P. J., *J. Phys. Coll. Chem.* **55**, 221 (1951).
- ⁴⁸ Bueche, F., *J. Chem. Phys.* **21**, 1850 (1953).
- ⁴⁹ Ferry, J. D., "Viscoelastic Properties of Polymers", John Wiley & Sons, Inc., New York, 1961, p. 201ff. (References).
- ⁵⁰ Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.* **77**, 3701 (1955).
- ⁵¹ Williams, M. L., *J. Phys. Chem.* **59**, 95 (1955).
- ⁵² Bueche, F., *J. Chem. Phys.* **24**, 418 (1956).
- ⁵³ Bueche, F., *J. Chem. Phys.* **30**, 748 (1959).
- ⁵⁴ Ferry, J. D. and others, *J. Colloid Sci.* **12**, 53 (1957).

THE **V**ANDERBILT LABORATORY

Located in East Norwalk, Connecticut.



... Maintained as a development and technical service center in the interest of our customers and their efficient use of Vanderbilt materials for Dry Rubber, Latex and Plastics Compounding.

TRIMATE M

New liquid latex accelerator

Developed by Vanderbilt research, and manufactured in our Bethel, Conn. plant.

This is a powerful dithiocarbamate accelerator with activity comparable to ETHYL ZIMATE. No preparation for compounding is required, and cold weather shipment is no problem.

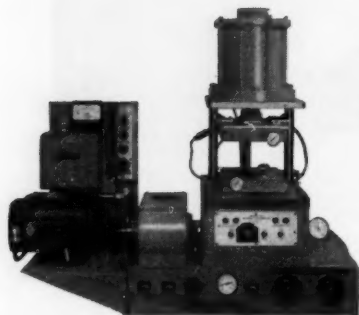
Write or contact your Vanderbilt technical representative for a sample and information.

R. T. VANDERBILT CO., INC.

230 Park Avenue, New York 17, N. Y.

VARIABLE SPEED MOONEY VISCOMETER

PROVIDES A RANGE OF SHEARING RATES



Scott Model STI Mooney Viscometer is now available with a variable speed drive unit to permit measurement of viscosity at different rates of shear . . . to provide required test data for control in the manufacture and use of plastic and high molecular weight elastomers, in conformance with ASTM Designation D1646 (formerly D927 and D1077), ISO, Governmental and industry standards.

New Variable Speed Drive offers shear rates from .05 to 20 RPM without stopping the test . . . and includes a tachometer for convenience in rate setting. This unit is a modification of the world-standard Scott Model STI Mooney Viscometer, known and accepted as a must for economical operation and the production of high quality products.



Precise Temperature Control within $\pm \frac{1}{2}^{\circ}\text{F}$ at any set temperature to 400°F is another important feature of the Scott Model STI. Designed and constructed for fast, easy calibration, effortless operation, and a modicum of maintenance . . . the new Variable Speed Viscometer may also employ Scott's new *dual-pen* recorder which simultaneously records viscosity in Mooney units and temperature of test specimen in $^{\circ}\text{F}$, on *one* chart.

Write today for full details on the Variable Speed Model STI. Scott Testers, Inc., 102 Blackstone St., Providence, Rhode Island. Tel.: DEXter 1-5650 (Area Code 401).

SCOTT TESTERS

THE SURE TEST . . . SCOTT



On-the-job literature for Rubber Men

RUBBER AGE

The industry's outstanding technical journal covering the manufacture of rubber and rubberlike plastics products.

SUBSCRIPTION RATES

	U.S.	Canada	Other
1 year	\$ 5.00	\$ 5.50	\$ 6.00
2 years	7.50	8.50	9.50
3 years	10.00	11.50	13.00
Single copies (up to 3 months)	50¢		
Single copies (over 3 months)	75¢		

RUBBER RED BOOK

Contains complete lists of rubber manufacturers and suppliers of materials, chemicals, equipment, services, etc. Now published on an annual basis. PRICE: \$15.00 per copy, domestic; \$16.00, overseas.

THE RUBBER FORMULARY

The "pharmacopeia" for rubber—providing all the rubber compounds published in technical journals and suppliers' releases. Each compound on a separate card with marginal indexes for various physical properties, type of hydrocarbon, etc. A simple mechanical system permits you to select compounds keyed to any property. Issued monthly. Back issues available. PRICE: \$95.00 per year.

STARTER SET

A Starter Set on The Rubber Formulary is also now available. It contains 2365 rubber compounds selected from the more than 9100 published in the Formulary in the years 1948 through 1957, inclusive. The formulas are presorted by polymer and then further subdivided for the convenience of the compounder. PRICE: \$250.00 per set.

ADHESIVES AGE

The first and only magazine to provide urgently needed information about the chemistry, manufacture, use and application of adhesives. News of new products, new techniques, new methods and new materials—all offering opportunities for growth, expansion, sales and profits. Easy to read . . . to use . . . practical . . . filled with useful ideas you can put to work. Subscriptions: \$5.00 per year, domestic; \$6.00 overseas.

PALMERTON PUBLISHING CO., INC.

101 West 31st St., New York 1, N. Y.

HERE'S HOW WITCO-CONTINENTAL PROTECTSYOUR **CARBON BLACK** DOLLAR
THROUGH

*Quicker, More Dependable Shipments • Unmatched Care in Packaging
Outstanding Loading and Stacking Techniques
Faster, Cleaner Unloading and Handling*

**CARBON BLACKS . . . PRODUCED AND HANDLED
WITH CARE BY WITCO-CONTINENTAL**

Only Witco-Continental gives carbon blacks such kid-glove treatment in packaging and shipping. There's no compromise on quality and no compromise on service. Facilities are maintained in

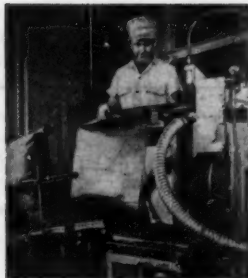
every sales office city for ex-warehouse customers. For outstanding service and personalized attention on all your carbon black orders . . . be sure to specify WITCO-CONTINENTAL.



There's less chance of shipping delay with Witco-Continental carbon blacks. We print your purchase order number, code or pigment number, type of black and other information, on every bag. Result is easier inventory, checking and handling.

Improved packing and better palletizing are achieved through specially built bag-shaping machines. You choose the type of bag you want.

Valve bags mean better unit loading, cleaner warehousing, faster and easier handling. Witco-Continental's exclusive, patented valve-filling machines insure greater uniformity of outside bag dimensions.





When carbon blacks leave Witco-Continental plants, you can be sure they're in good condition. We photograph each shipment after loading as a check on correct and damage-free stacking. These photographs, with specially designed loading diagrams attached, are then sent to you as your check on shipping conditions.



Special ear liners prevent interlocking of bags and protect them from each other and from the sides of cars or trailers. Convenient, disposable pallets facilitate handling, yet eliminate storage or return costs.



If you prefer shipment by hopper car, Witco-Continental traffic control system means that you can get same-day information on the whereabouts of your shipment from your local sales office. There are 113 carefully maintained hopper cars ready to serve you.



WITCO CHEMICAL COMPANY, Inc.
CONTINENTAL CARBON COMPANY

122 East 42nd Street, New York 17, N. Y.

Chicago • Boston • Akron • Atlanta • Houston • Los Angeles
San Francisco • London and Manchester, England



THINK *Thiokoe*

for worthy work
and
leisurely living

PHYSICAL TEST DEVELOPMENT CHEMIST

To develop methods of physical test for evaluation of solid propellant and propellant materials. These tests include tensile testing, particle size measurement, determination of burning rates, specific impulse, and other related areas.

Requirements—Science degree in Engineering, Physics, or Chemistry, with at least two years pertinent laboratory experience.

ANALYTICAL CHEMIST

To develop methods of chemical testing of solid propellant, raw materials, and solid propellant formulations. Requirements—Degree in Chemistry, with four or more years of experience in analytical instrumentation and at least two years direct experience in gas chromatographic methods.

Most workers who come to this northern Utah area enjoy it. Probably you will too. There's so much to see and enjoy. Living can be exciting or leisurely, as you like it.

Send resume to Noel Murray,
Employment Supervisor
DEPT. X290

Thiokoe[®]

CHEMICAL CORPORATION

120 S. MAIN STREET, BRIGHAM CITY, UTAH

AN EQUAL OPPORTUNITY EMPLOYER

ADVERTISE *in*

RUBBER CHEMISTRY AND TECHNOLOGY

KEEP YOUR NAME AND
YOUR PRODUCTS CON-
STANTLY BEFORE THE
RUBBER TECHNOLOGIST

Advertising rates and information about available locations may be obtained from George Hackim, Advertising Manager, Rubber Chemistry and Technology, care of The General Tire & Rubber Company, Chemical Division, Akron 9, Ohio

ENJAY BUTYL

best way to handle electricity



Enjoy Butyl withstands all the common foes of electrical insulation—heat, water, corona, ozone, sun, weather, and high-voltage discharge. Because of its exceptional heat resistance, Butyl-insulated cable lets you carry a higher current with a given conductor size. Water absorption of Butyl insulation at 90°C is only about one-sixth that of conventional compounds, making it ideal for underground and underwater applications.

Butyl's high dielectric strength prevents excessive loss (with its resultant

cable deterioration and increase in transmission cost); also guards against breakdowns due to surge currents. These characteristics have made Enjoy Butyl the preferred rubber for insulation of power cable, transformers and busbars. Coupled with outstanding abrasion resistance, these same characteristics point the way toward increased use of Butyl as a jacketing material.

For more information, write to Enjoy, 15 West 51st Street, New York 19, New York.

EXCITING NEW PRODUCTS THROUGH PETRO-CHEMISTRY

ENJAY CHEMICAL COMPANY

A DIVISION OF HUMBLE OIL & REFINING COMPANY



**RUBBER CHEMISTRY AND TECHNOLOGY
IS SUPPORTED BY ADVERTISING
FROM THESE LEADING SUPPLIERS**

INDEX TO ADVERTISERS

	PAGE
American Cyanamid Company, Rubber Chemicals Division.	12
American Zinc Sales Company. (Opposite Inside Back Cover)	30
Cabot Corporation. (Opposite Inside Front Cover)	1
Carter Bell Manufacturing Company.	28
Columbian Carbon Company. (Opposite Title Page)	
DPR, Incorporated.	25
DuPont, E. I., de Nemours & Company, Inc.	9
Eastman Chemical Products, Inc.	6
Enjay Chemical Company.	23
General Tire & Rubber Company, Chemical Division.	10
Goodrich, B. F., Chemical Company.	13
Goodyear Tire & Rubber Company, Chemical Division.	5
Hall, C. P., Company.	25
Harwick Standard Chemical Company. (Inside Back Cover)	
Huber, J. M., Company.	27
Naugatuck Chemical Division (U. S. Rubber Company) Rubber Chemicals.	8
Ozone Research & Equipment Corporation.	7
Pacific Smelting Company. (Outside Back Cover)	
Phillips Chemical Company (Philblack).	4
Phillips Chemical Company (Philprene).	16
Rubber Age.	19
Rubber World.	28
St. Joseph Lead Company.	29
Scott Testers, Inc.	18
Southern Clays, Inc.	26
Thiokol Chemical Corporation.	22
United Carbon Company. (Inside Front Cover)	
Vanderbilt, R. T., Company.	17
Witco Chemical Company, Inc.	20-21

*Call
Hall*

for
Laboratory Reagents

Fast Service . . Glassware, Thermometers,
Hydrometers and Microscopes.

JE 5-5175

for
**Laboratory
Design Service**

Complete Laboratory Design Service . . . Fume
Hoods, Lab Tables, Microscope Tables, etc.

JE 5-5175



AKRON CHICAGO MEMPHIS
LOS ANGELES NEWARK

The C. P. Hall Co.
CHEMICAL MANUFACTURERS



DPR[®]

DEPOLYMERIZED RUBBER

**NATURAL CRUDE RUBBER IN
LIQUID FORM — 100% SOLIDS**

Available in HIGH and LOW VISCOSITIES



INCORPORATED

A SUBSIDIARY OF
H. V. HARDMAN CO., INC.

595 CORTLANDT STREET
BELLEVILLE 9, N. J.

NOW!
ROOM
TEMPERATURE
VULCANIZING
for
DPR
(no sulphur)





4
OUTSTANDING
PRODUCTS

WHITETEX
A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA
A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO
A tried and proved product for compounding rubber and synthetic rubber.

No. 33 CLAY
For wire and vinyl compounding

For full details, write our
Technical Service Dept.

Southern Clays, Inc.

33 RECTOR STREET,

NEW YORK 6, N. Y.

CARBON BLACKS

Wyex EPC

Easy Processing Channel Black

Arrow MPC

Medium Processing Channel Black

Essex SRF

Semi-Reinforcing Furnace Black

Modulux HMF

High Modulus Furnace Black

Aromax CF

Conductive Furnace Black

Aromax HAF

High Abrasion Furnace Black

Aromax ISAF

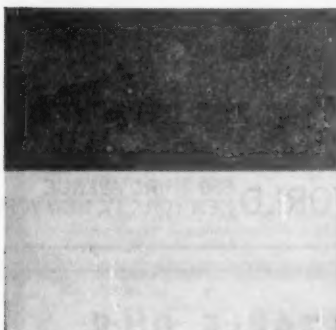
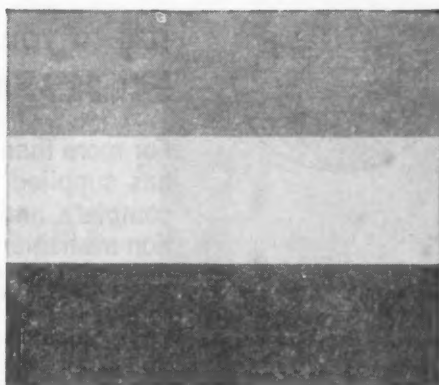
Intermediate Super Abrasion Furnace Black

Arovel FEF

Fast Extruding Furnace Black

Arogen GPF

General Purpose Furnace Black



CLAYS

Suprex Clay

High Reinforcement

Paragon Clay

Easy Processing

Hi-White R

White Color

LGB

Very low grit, high reinforcement

LGP

Very low grit, easy processing

Polyfil C, X* and F*

Fine particle, light color, water fractionated

*also available in spray-dried form



RUBBER CHEMICALS

Turgum S, Turgum SB

Natac

Butac

Resin-Acid Softeners

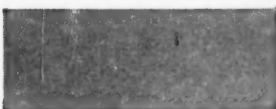
Aktone

Accelerator Activator

Zeolex 23*

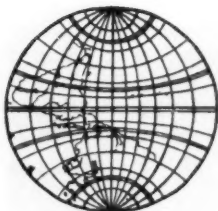
White Reinforcing Pigment

*also available in spray-dried form



J. M. HUBER CORPORATION

630 Third Avenue, New York 17, N. Y.



it's to your advantage to read
RUBBER WORLD

For more than 72 years RUBBER WORLD has supplied its industry with the most complete and up-to-the-minute information available. RUBBER WORLD is a basic part of the rubber industry, just as rubber is a vital and basic part of modern technology. This was never more true than today, when RUBBER WORLD leads its field in editorial innovation and in circulation vitality.

By any comparison, RUBBER WORLD is the dominant book.

RUBBER WORLD 630 THIRD AVENUE
NEW YORK 17, NEW YORK

VULCANIZED VEGETABLE OILS
• RUBBER SUBSTITUTES •



REPRESENTED BY

HARWICK STANDARD CHEMICAL CO.

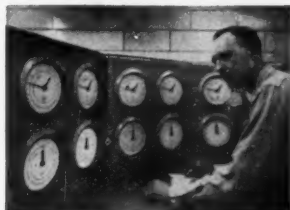
Akron — Boston — Trenton — Chicago — Denver — Pico Rivera (Cal.) —
Albertville (Ala.) — Greenville (S. C.)

ST. JOE**"Controlled-Analysis"**

ZINC OXIDES

For The

RUBBER INDUSTRY



Direct Reporting On Baird-Atomic Spectrometer

RUBBER GRADE — FAST CURING TYPES**ST. JOE No. 20**

Very fine particle size, giving maximum reinforcement and activation in rubber. For highest quality rubber goods.

ST. JOE No. 30

Excellent reinforcing and activating properties in rubber. Having fewer extremely fine particles, it is easier to incorporate than St. Joe No. 20.

RUBBER GRADE — SLOW CURING TYPES**ST. JOE No. 31**

Slow curing type for long flat cures and excellent scorch resistance. Good activating and reinforcing properties.

RUBBER GRADE — SURFACE TREATED TYPES**ST. JOE No. 20-21****ST. JOE No. 42-21**

These grades are made from St. Joe No. 20 and St. Joe No. 42, respectively, by surface treating with a nontoxic hydrophobic high molecular weight organic

ST. JOE No. 42

General purpose type. Excellent activating and moderate reinforcing properties. Faster rate of incorporation into rubber than St. Joe No. 20 or St. Joe No. 30.

ST. JOE No. 43

Large particle size type for easy incorporation. Good activating and reinforcing properties.

ST. JOE No. 42A-3

Somewhat larger in particle size than St. Joe No. 31 for easier incorporation; otherwise, similar in general characteristics.

material. They disperse in a rubber mix rapidly and thoroughly, developing physical properties, in vulcanized rubber comparable to standard St. Joe No. 20 and St. Joe No. 42.

LATEX GRADE**ST. JOE No. 20**

Very fine particle size, giving minimum settling out in water dispersions and maximum activation in Latex Compounds.

ST. JOE No. 12

Heavily calcined St. Joe No. 20 type, containing few extremely fine particles. Less reactive than St. Joe No. 20 and produces low viscosity water dispersions which do not readily thicken.

ST. JOE No. 43

Medium particle size for easy wetting. In pellet form this grade is particularly advantageous in preparing pourable 70% zinc oxide water dispersions.

ST. JOE No. 46

Low pH type used in foam latex where zinc oxide is used for both activation and as a supplementary gelling agent.

ST. JOE No. 30

Intermediate particle size, having fewer extremely fine particles than St. Joe No. 20. Less reactive than St. Joe No. 20, producing lower viscosity water dispersions which do not readily thicken.

ZNO-1222A



St. Joe's Distributor Network Puts St. Joe ZnO On Your Doorstep.

ARROW, O.
ALBANYVILLE, ALA.
BALTIMORE, MD.
BOSTON, MASS.
BUFFALO, N. Y.
CHICAGO, ILLINOIS
CHICAGO, ILLINOIS
DALLAS, TEX.

DENVER, COLO.
DETROIT, MICH.
GREENVILLE, S. C.
HOUSTON, TEX.
HUNTINGTON, W. VA.
JACKSONVILLE, FLA.
KANSAS CITY, MO.
LITTLE ROCK, ARK.

LONG ISLAND CITY, N. Y.
LOS ANGELES, CAL.
MEMPHIS, TENN.
OKLAHOMA CITY, OKLA.
OMAHA, NEB.
PHILADELPHIA AREA, PA.
PITTSBURGH AREA, PA.
PORTLAND, ORE.

ST. LOUIS, MO.
ST. PAUL, MINN.
SAN ANTONIO, TEX.
SAN FRANCISCO, CAL.
SEATTLE, WASH.
TRENTON, N. J.
TULSA, OKLA.
WICHITA, KAN.

Write for the name of the St. Joe distributor nearest you.

ST. JOSEPH LEAD CO.

250 Park Avenue • New York 17, N. Y.

Plant & Laboratory: Josephstown (Monaca) Pa.

ZNO-1222 B

Now You Can Greatly Increase Warehouse Space
at No Increase in Cost With...
AZODOX... High Apparent Density Zinc Oxides



- Easier to Handle
- Stacks Higher, Safely
- Less Bag Breakage
- Close-Packed, Unitized Shipments

AZODOX stores in much less space than other zinc oxides. That's because you get many more pounds of AZODOX per cubic foot of pigment—up to 62 lbs. per cubic foot! Save valuable space for other purposes with every ton of AZODOX you buy.

In the manufacture of AZODOX, an exclusive process removes excess, space-wasting air from between individual particles of zinc oxide. Actual pigment density and every other desirable property remain unchanged. High apparent density AZODOX flows freely yet dusts less, incorporates fast and disperses thoroughly.

AZODOX is available in the following grades at no additional cost over conventional zinc oxides:

	Bulk Density lbs./cu. ft.	Rate of Activation	Reinforcement Properties
AZODOX-44 (Conventional)	60	Medium	High
AZODOX-55 (Conventional)	60	Fast	High
AZODOX-55-TT (Surface Treated)	62	Fast	High
AZODOX-550 (Conventional)	58	Medium	High

For technical data, fill in and mail this coupon.

American Zinc Sales Company
1515 Paul Brown Bldg.
St. Louis 1, Mo.

Please send me technical information about

- ☐ AZODOX-44 ☐ AZODOX-55-TT
☐ AZODOX-55 ☐ AZODOX-550
☐ 15 types of AZO brand zinc oxides

Name..... Title.....

Company.....

Address.....

City..... Zone..... State.....

American
Zinc sales co.

Distributors for
AMERICAN ZINC, LEAD AND SMELTING CO.
Columbus, Ohio • Chicago • St. Louis • New York

